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THE PHOTOCHEMISTRY OF SOME ACYCLIC KETONES CONTAINING A SILICON OR A TIN ATOM

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THE PHOTOCHEMISTRY OF SOME ACYCLIC KETONES CONTAINING A SILICON OR A TIN ATOM

BY

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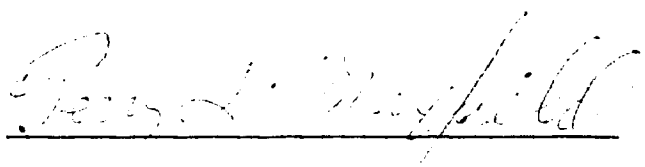


TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

The photolysis of ketones in the gaseous phase has been widely studied. Acetone is an example of a ketone which has been investigated considerably. Noyes and Dorfmann[1] proposed the following generally accepted free radical mechanism for the photolysis of acetone.

$$CH_3COCH_3 \xrightarrow{h\nu} CH_3\dot{C}O + CH_3\cdot \quad (1)$$

$$CH_3\dot{C}O \longrightarrow CH_3\cdot + CO \quad (2)$$

$$2\ CH_3\cdot \longrightarrow C_2H_6 \quad (3)$$

$$2\ CH_3\dot{C}O \longrightarrow (CH_3CO)_2 \quad (4)$$

$$CH_3\cdot + CH_3COCH_3 \longrightarrow CH_4 + CH_3\dot{C}OCH_2 \quad (5)$$

$$CH_3\cdot + CH_3\dot{C}OCH_2 \longrightarrow CH_3COC_2H_5 \quad (6)$$

$$2\ CH_3\dot{C}OCH_2 \longrightarrow (CH_3COCH_2)_2 \quad (7)$$

$$CH_3\dot{C}OCH_2 \longrightarrow CH_3\dot{} + CH_2CO \quad (8)$$

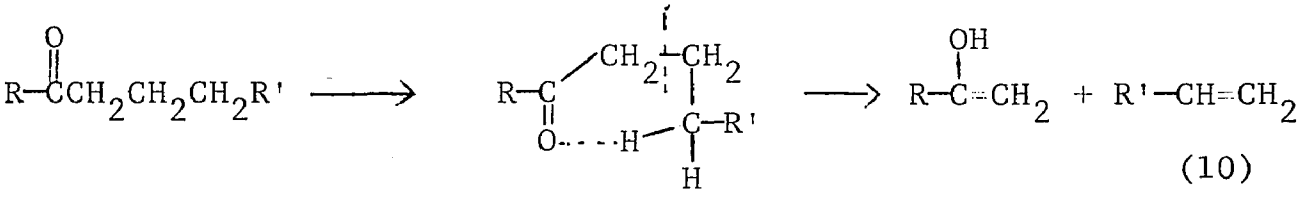
(only at higher temperatures)

All of the products shown have been isolated from the reaction mixture. Dorfmann and Sheldon[2] have shown that diethyl ketone also gives similar results.

However, when a chain of three or more carbons compose one of the groups on the ketone, a different mechanism appears. This was first shown by Bloch and Norrish[3] when they photolysed 2-hexanone and found acetone and propylene to be the major products.

$$CH_3CO(CH_2)_3CH_3 \xrightarrow{h\nu} CH_3COCH_3 + C_3H_6 \quad (9)$$

Similar results have been obtained for di-n-propyl ketone,[4,5] methyl n-propyl ketone, methyl n-amyl ketone and methyl sec-butyl ketone.[6] Davis and Noyes[7] suggested a mechanism which has been widely accepted. It involves the cleavage of the carbon-carbon bond once removed from the carbonyl with the migration of a hydrogen on the γ-carbon atom to the carbonyl oxygen, and is often referred to as the Norrish Type II mechanism.



(10)

Several pieces of evidence have been reported to substantiate this mechanism[6]: (a) the olefin from methyl n-amyl ketone is 1-butene, (b) ketones such as methyl iso-propyl ketone with no γ-hydrogen do not undergo this reaction (the mechanisms in these cases are similar to that of acetone), (c) methyl sec-butyl ketone gives ethylene and methyl ethyl ketone rather than propene and acetone.

The nature of the complex photolysis of longer chain ketones was shown by Ausloos and Murad.[8] In the photolysis of 2-pentanone-1,1,1,3,3,-d_5, the products isolated indicate that the following free radical reactions had occurred:

$$CD_3COCD_2CH_2CH_3 \longrightarrow CD_3COCD_2H + C_2H_4 \quad (11)$$

$$\longrightarrow CD_3\cdot + \cdot COCD_2CH_2CH_3 \quad (12)$$

$$\longrightarrow CD_3\dot{C}O + \cdot CD_2CH_2CH_3 \quad (13)$$

$$CH_3CH_2CD_2\dot{C}O \longrightarrow CH_3CH_2CD_2\cdot + CO \quad (14)$$

$$CD_3\dot{C}O \longrightarrow CD_3\cdot + CO \quad (15)$$

$$CD_3\dot{C}O + \cdot CD_2CH_2CH_3 \longrightarrow CD_3COCD_2CH_2CH_3 \quad (16)$$

$$\longrightarrow \quad CD_3CHO + CD_2{=}CHCH_3 \qquad (17)$$

$$\longrightarrow \quad CD_2CO + CD_3CH_2CH_3 \qquad (18)$$

$$2\cdot CD_2CH_2CH_3 \longrightarrow (CH_3CH_2CD_2)_2 \qquad (19)$$

$$\longrightarrow \quad CH_3CH_2CD_2H + CD_2{=}CHCH_3 \qquad (20)$$

$$2\ CD_3\dot{C}O \longrightarrow (CD_3CO)_2 \qquad (21)$$

$$\longrightarrow \quad CD_3CDO + CD_2CO \qquad (22)$$

$$CD_3^{\cdot} + CH_3CH_2CD_2^{\cdot} \longrightarrow CD_3CD_2CH_2CH_3 \qquad (23)$$

$$\longrightarrow \quad CD_3H + CD_2{=}CHCH_3 \qquad (24)$$

$$CD_3^{\cdot} + CD_3\dot{C}O \longrightarrow CD_3COCD_3 \qquad (25)$$

$$\longrightarrow \quad CD_4 + CD_2CO \qquad (26)$$

$$2\ CD_3^{\cdot} \longrightarrow C_2D_6 \qquad (27)$$

Only two products were obtained in large quantities: ethylene and pentadeurioacetone. The other products were obtained only in minute quantities.

In solution photochemistry, the reaction possibilities are even more complex. The solvent itself can take part in the reactions. A good example is the photolysis of acetone in a hydrocarbon solvent. It has been reported that no gases are given off in the liquid phase photolysis.[9] Yang and Yang[10] reported that the photolysis of acetone in cyclohexane gave 2-propanol and other products of free radical reactions which involve the cyclohexane as well as the ketone.

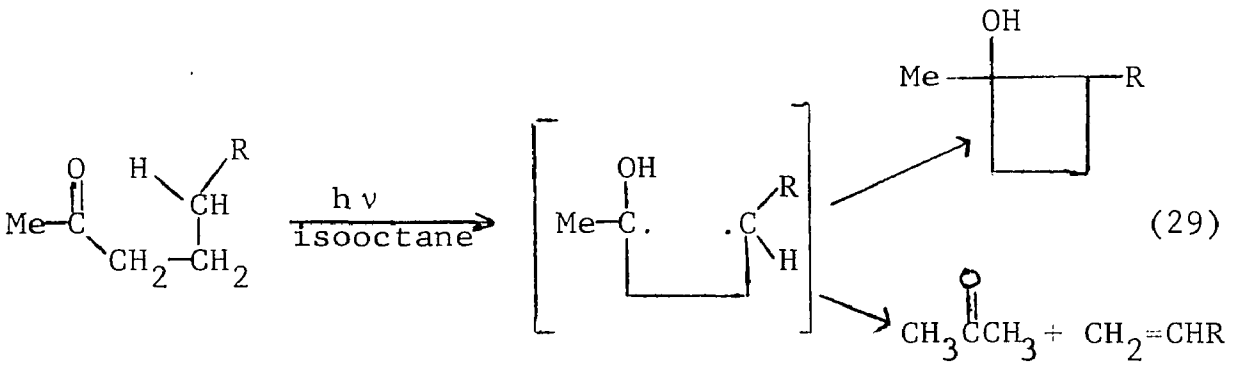
$$CH_3COCH_3 \xrightarrow[\text{cyclohexane}]{h\nu} \underset{53\%}{CH_3CHOHCH_3} + \underset{12\%}{C_6H_{11}COH(CH_3)_2} + \qquad (28)$$

$$\underset{8\%}{CH_3CO(CH_2)_2COCH_3} + \underset{15\%}{CH_3COCOCH_3} + \text{cyclohexylcyclohexene} + \text{hydrocarbon polymers.}$$

The involvement of the cyclohexane is revealed by the nature of

the products. The solvent functions as a source of the hydrogen atom. The cyclohexyl radical formed can then couple with other radicals which are in the solution.

With ketones containing more than three carbons in one chain, the Norrish Type II reactions occur with the formation of lower molecular weight ketones and olefins. However, there is one additional reaction which has been observed. This reaction leads to the formation of cyclobutanols. Yang and Yang[10] examined the photolysis of several ketones and suggested a diradical intermediate.



(29)

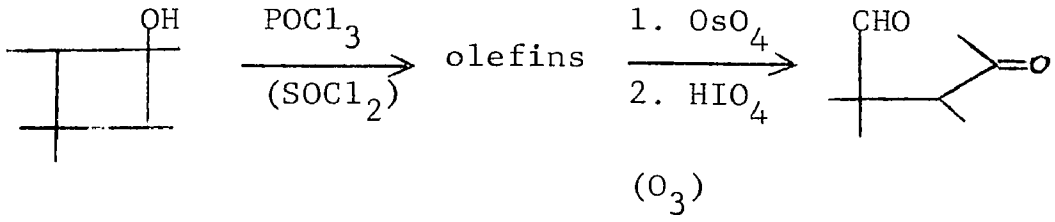
Table I shows the product distribution in three cases.

TABLE I

Cyclobutanol Formation in Photolysis

R	Yield Cyclobutanol	Yield olefin and ketone
H	12%	-
C_3H_7	17%	67%
C_4H_9	10%	60%

The structure of the four-membered rings were determined by degradation. First, the alcohol was dehydrated using phosphorus oxychloride or thionyl chloride. The olefin was oxidized with either osmium tetroxide and metaperiodic acid or ozone. The carbonyl compounds were then identified by comparison with authentic samples,



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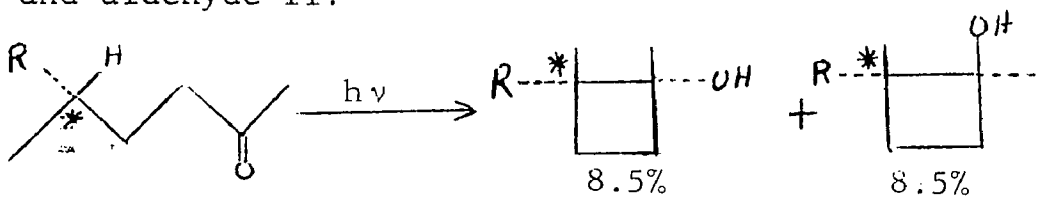
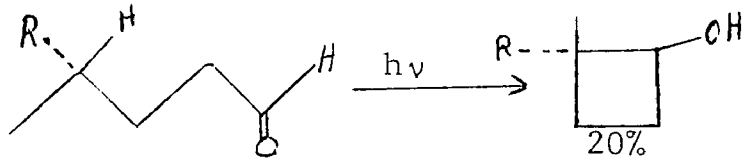
Further examples of the formation of the cyclobutanols were reported by Orban and co-workers[11] in the photolysis of ketone I and aldehyde II.



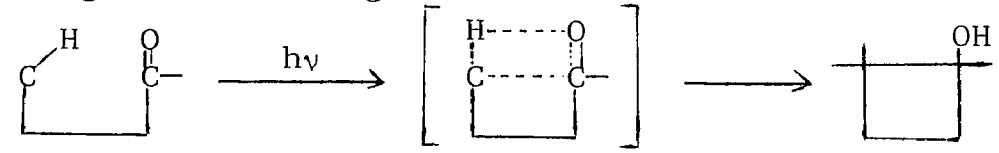
(31)

R = $(CH_2)_3CHMe_2$



(32)

They point out that the data available does not exclude a concerted mechanism, eq. (33). They also obtained evidence that the optically active ketones gave partial retention of configuration during the reaction.



(33)

Further work needs to be done before this mechanism is well understood.

STATEMENT OF PROBLEM

In the last few pages, several photochemical reactions of ketones have been reviewed. One with interests in organometallic chemistry might find it very intriguing to determine the effect a metal or metaloid atom in the molecule being photolysed might have on the reactions. Possibilities are quite extensive as there are a number of metals which form stable compounds. The metals and metaloids of groups IVA and VA are examples. Also, the position of the hetero atom in the molecule can be varied with respect to the carbonyl group.

Organotin and organosilicon compounds were chosen for the present research. The position of the hetero atom was varied with respect to the carbonyl by varying the number of methylene carbons between them.

$$Me_3M(CH_2)_xCOR$$

x=0,1,2, etc. R= Me or Ph
M = Si or Sn

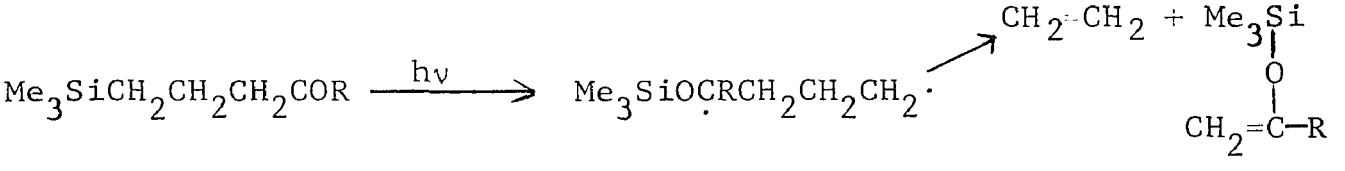
Only phenyl and methyl ketones were studied in this series. The purpose of the research was to determine how the photochemistry varied with the nature of M and R; and the magnitude of x. One factor which might affect the behavior of these molecules is the relative magnitude of bond energies. Table II gives some pertinent values.

TABLE II

Bond Energies in kcal./mole[12]

Bond	Energy	Bond	Energy
C-C	82.6	Si-Cl	91
Si-C	76	C-H	98.7
C-O	84.0	Si-H	76
Si-O	108	Sn-C[13]	54
C-Cl	81	O-H[14]	110.6

A consideration of the bond energies would bear on the question of whether the excited oxygen would form a bond with the γ-hydrogen or the γ-silicon.



(34)

Calculations of the thermochemical extraction of a hydrogen by the excited oxygen in a Norrish Type II reaction indicate that the reaction should be exothermic by about 12 kcal./mole.

O-H formation 110.6 kcal./mole

C-H breaking -98.7

11.9 kcal./mole

Now, the calculation for the reaction in which a silicon atom would be extracted rather than a hydrogen atom is much more exothermic, giving a value of 32 kcal./mole.

O-Si formation	108 kcal./mole
Si-C breaking	-76
	32 kcal./mole

According to this, one would expect the silicon-oxygen bond to form over the hydrogen-oxygen bond. However, this is an oversimplified picture and other factors, such as steric effects, might affect the course of the reaction.

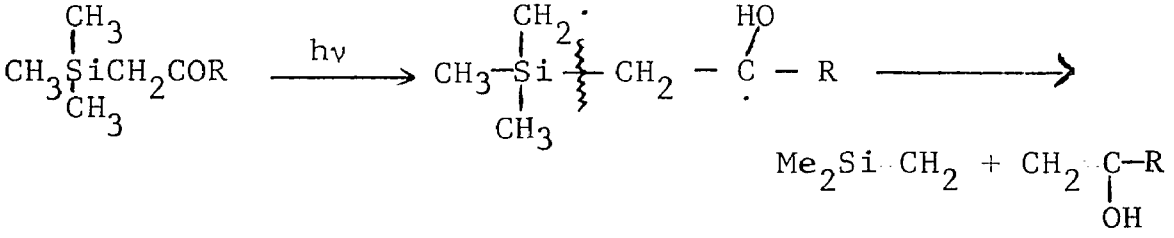
Another question regarding the bond energies involves the transfer of energy from the excited carbonyl group as vibrational and rotational energy or otherwise to the metal-carbon bond causing cleavage.

$$Me_3M(CH_2)_xCOR \xrightarrow{h\nu} Me_3M. + \cdot(CH_2)_xCOR \qquad (35)$$

M= Sn or Si x 1,2,3 etc. R CH_3 or Ph

The tin-carbon bond is weaker than the silicon-carbon bond, and it would be expected to cleave more readily.

Another point for consideration is whether the oxygen atom in an excited carbonyl would remove an α-hydrogen from the methyl group on the metal or metaloid atom forming a radical which could then form a methylene silicon compound.



(36)

This reaction would be quite interesting as no stable compounds with silicon-carbon double bonds are known. No doubt further possible reactions can be conceived, but these few examples will suffice to give some indication of reactions which might

be expected.

To the present, little work has been done on the photolysis of organotin or silicon compounds. Some work has been done with organotin halides and with reactions of tetraalkyltin compounds with organic halides. Razuvaev and co-workers[15] photolysed tetraethyltin in chloroform and also in bromopropane obtaining gases and organotin halides as products.

$$Et_4Sn + CCl_4 \xrightarrow[8\ hrs.]{h\nu} C_2H_6 + C_2H_4 + Et_3SnCl + Et_2SnCl_2 \qquad (37)$$

$$Et_4Sn + C_3H_7Br \xrightarrow{h\nu} C_2H_6 + C_2H_4 + C_3H_8 + Et_3SnBr + Et_2SnBr_2 \qquad (38)$$

Triethyltin chloride itself reacts photochemically.

$$Et_3SnCl \xrightarrow[90\ hrs.]{h\nu} C_2H_6 + C_2H_4 + Et_2SnCl_2 + Sn + SnCl_2 \qquad (39)$$

RESULTS AND DISCUSSION

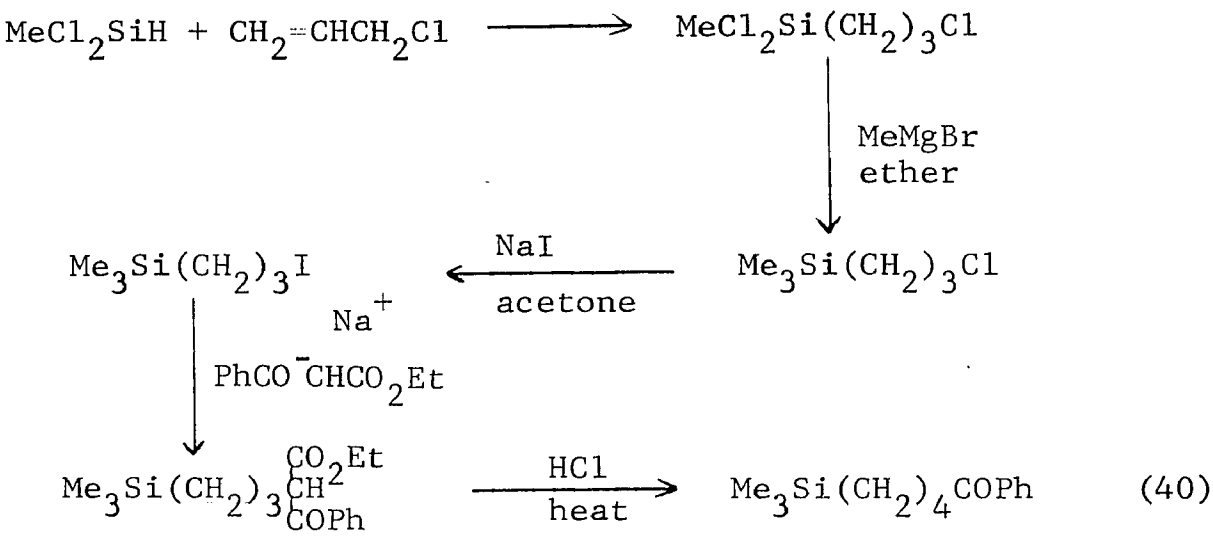
The primary purpose of this research was to explore the photochemistry of several ketones containing tin and silicon atoms. Each compound will be discussed separately and comparison will be made where appropriate. The discussion will be divided into three general sections. First, the silicon compounds will be considered starting with the larger molecules, then the tin compounds, and finally some unsuccessful attempts to prepare ketones for photolysis.

General Procedures

The photochemical work was carried out according to three different procedures. The first procedure (a) involved the photolysis of the highly diluted (90-95% solvent) ketone in total volumes of 170 ml. The lamp and cooling unit were immersed in the solution to be photolysed. (see Figure in Experimental section). In the second, procedure (b), samples of the order of 10-30 millimoles were photolysed in capillary tubes immersed in a water bath. (see Figure in Experimental section). The third, procedure (c), was similar to the second except the samples were photolysed in a degassing apparatus (Figure 3). The samples were degassed before photolysis unless otherwise noted.

A. 2-Sila-2,2-dimethyl-7-phenylheptan—7-one (III)

The longest chain compound to be studied in this work was 2-sila-2,2-dimethyl-7-phenylheptan—7-one, $Me_3Si(CH_2)_4COPh$. The preparation of this compound was carried out according to the method of Sommer and co-workers[16] except for the last two steps.



When the benzoylacetate was heated with concentrated hydrochloric acid, decarboxylation did not occur. Most of the starting material was recovered along with some acetophenone. However, decarboxylation was achieved by warming the ester with a solution of potassium hydroxide in aqueous ethanol.

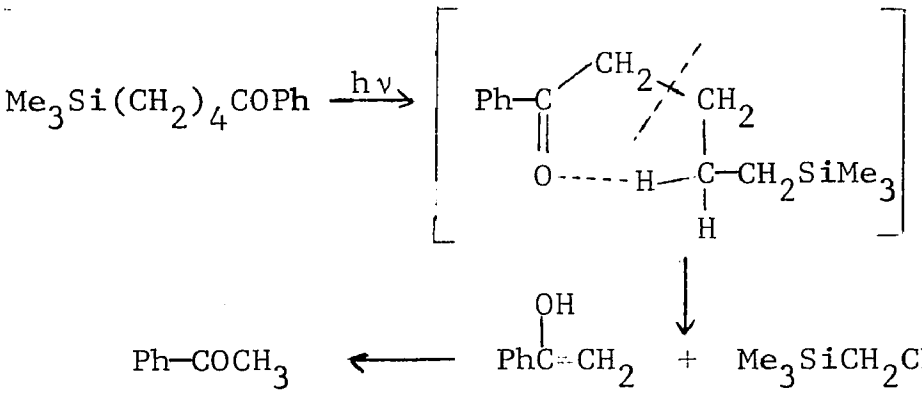
The 2-Sila-2,2-dimethyl-7-phenylheptan-7-one was photolysed in small quartz tubes which were sealed either by rubber policemen or by fusion. The irradiations were carried out with the General Electric 400 watt lamp according to procedure (b). The results are given in Table III. In all cases the ketone had almost completely reacted. The products were separated by gas-liquid chromatography using the silicone oil 200 on haloport F column. Comparison of the infrared spectra of the products was made with spectra of the known compounds for identification of products. The remainder of the products was polymeric material which was not examined further. The infrared spectrum of the photolysed mixture indicated the presence of a small amount of alcohols of undetermined structure.

TABLE III

Photolysis of 2-Sila-2,2-dimethyl-7-phenylheptan-7-one

No.	Solvent	Time (hrs.)	Percent yield $Me_3SiCH_2CH=CH_2$	Percent yield PhCOMe
1	40% cyclohexane	31	58	-
2	neat	24	65	-
3	31% cyclohexane	24	-	61
4	30% "	24	-	57
5	34% "	4.5	58	52
6	30% "	6.0	67	57

The formation of acetophenone and allyltrimethylsilane in large yield suggests the Norrish Type II mechanism in which ketones with hydrogens gamma to the carbonyl cleave to give ketones and olefins. This mechanism has been shown to apply to aliphatic ketones and may apply to aromatic ketones. To the author's knowledge it has not previously been reported that phenyl ketones undergo the Norrish Type II reaction.



(41)

B. 2-Sila-2,2-dimethyl-6-phenylhexan-6-one (IV)

If one methylene carbon is removed from the chain of compound III, the new compound is 2-sila-2,2-dimethyl-6-phenyl-hexan-6-one, $Me_3Si(CH_2)_3COPh$. This ketone was prepared by treating the corresponding nitrile with phenylmagnesium bromide.

$$MeCl_2SiH + CH_2{=}CHCH_2CN \xrightarrow{Pt/C} MeCl_2SiCH_2CH_2CH_2CN$$

$$\downarrow MeMgBr$$

$$Me_3Si(CH_2)_3COPh \xleftarrow[2.\ HCl,H_2O]{1.\ PhMgBr} Me_3Si(CH_2)_3CN \qquad (42)$$

This ketone was photolysed by two different methods. The first work was done in the large volume apparatus (runs 1-3) as described in procedure (a) in the Experimental section. The remainder of the work was done in small quartz tubes (runs 4-5) using the General Electric 400 watt lamp. The results are given in Table IV. The yields of the acetophenone and vinyltrimethylsilane were determined by gas-liquid chromatography using both the Silicone oil 200 and the Apiezon L columns. The yield of the benzoylethane was determined by isolation.

Compounds III and IV react similarly, namely according to the Norrish Type II mechanism. This course would be anticipated because of the presence of the γ-hydrogen.

$$Me_3Si(CH_2)_3COPh \xrightarrow{h\nu} \left[\begin{array}{c} Ph-C(=O)-CH_2-CH_2-CH(-H\cdots O)-CH_2-SiMe_3 \end{array}\right] \downarrow$$

$$PhC(OH)=CH_2 + Me_3SiCH=CH_2 \qquad (43)$$

Here also the formation of alcohols was evident from the

TABLE IV

Photolysis of 2-sila-2,2-dimethyl-6-phenylhexan-6-one

No.	Solvent	Time (hrs.)	Percent[a] reacted	Procedure and Filter	Percent yield		
					$Me_3SiCH{=}CH_2$	PhCOMe	$(PhCOCH_2)_2$
1[b]	95% pentane	26.5	95-100	(a) no filter	lost	75%	-
2	96% heptane	12	100	(a) Vycor filter	66	-[c]	-
3	91% heptane	1.1	100	(a) Vycor filter	84	71	-
4	neat	4	95-100	(b) Vycor filter	69	75	10
5	20% cyclohexane	23	95-100	(b) Vycor filter	53	71	-
6	20% cyclohexane	29	95-100	(b) Vycor filter	95	65	13
7	20% cyclohexane	28	95-100	(b) Vycor filter	66	-	-

[a]The percentage is by weight. The remainder was ketone.

[b]The lamp was not working properly. It was not at full intensity.

[c]The sample was over irradiated, and 2,3-diphenyl-2,3-butanediol was the major product.

infrared spectrum of the reaction mixture, but only in small yield and no attempt was made at isolation.

C. 2-Sila-2,2-dimethylheptan-6-one (V)

The methyl ketone corresponding to compound IV is 2-sila-2,2-dimethylheptan-6-one, $Me_3Si(CH_2)_3COCH_3$. This compound was prepared according to the procedure of Sommer and co-workers.[16]

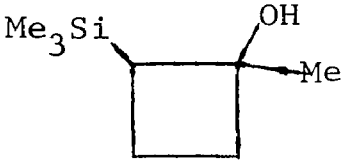
$$MeCl_2SiH + CH_2{=}CHCH_2CN \xrightarrow{Pt/C} MeCl_2Si(CH_2)_3CN \xrightarrow[2.\ HCl,H_2O]{1.\ MeMgBr} Me_3Si(CH_2)_3COCH_3 \quad (44)$$

The photolysis was carried out according to all three procedures, (a), (b), and (c). The conditions and results are given in Table V. The yields were determined by gas-liquid chromatography except for that of the alcohols in run No. 1. The latter were determined by conversion to 3,5-dinitrobenzoates and separation by column chromatography on a silica column. The 13% in run No. 1 represents the total yield for all the isomers from the reaction of the ketone with the solvent pentane. The presence of 2-sila-2,2,6,7-tetramethyldecan-6-ol, $Me_3Si(CH_2)_3CMe(OH)CHMe(CH_2)_2CH_3$, was indicated by comparison with authentic sample of the alcohol on a thin layer chromatogram and by identical infrared spectra of the 3,5-dinitrobenzoate ester. The structure of the cyclobutanol was indicated by oxidation of the dehydration product with potassium permanganate. The product obtained was levulinic acid.

TABLE V

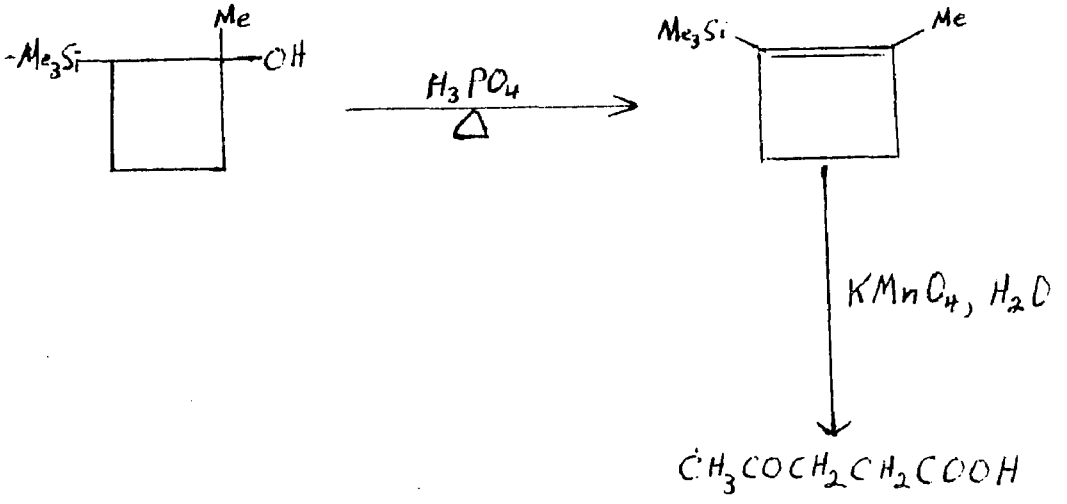
Photolysis of 2-sila-2,2-dimethylheptan-6-one

No.	Solvent[b]	Time (hrs.)	Percent reacted	Procedure and Filter
	Conditions			
1	87% pentane	9	85-90	(a) Vycor
2	24% cyclohexane	46	92	(b) Vycor
3	23% ethanol	32	90	(c) degassed
4	25% cyclohexane	46	90	(d) Vycor

		$Me_3SiCH{=}CH_2$	$Me_3Si(CH_2)_3CR(OH)Me$
	Percent yield		
No. 1	23-28%	Lost[a]	13
2	19	39	-
3	21	Lost[a]	-
4	20	42	-

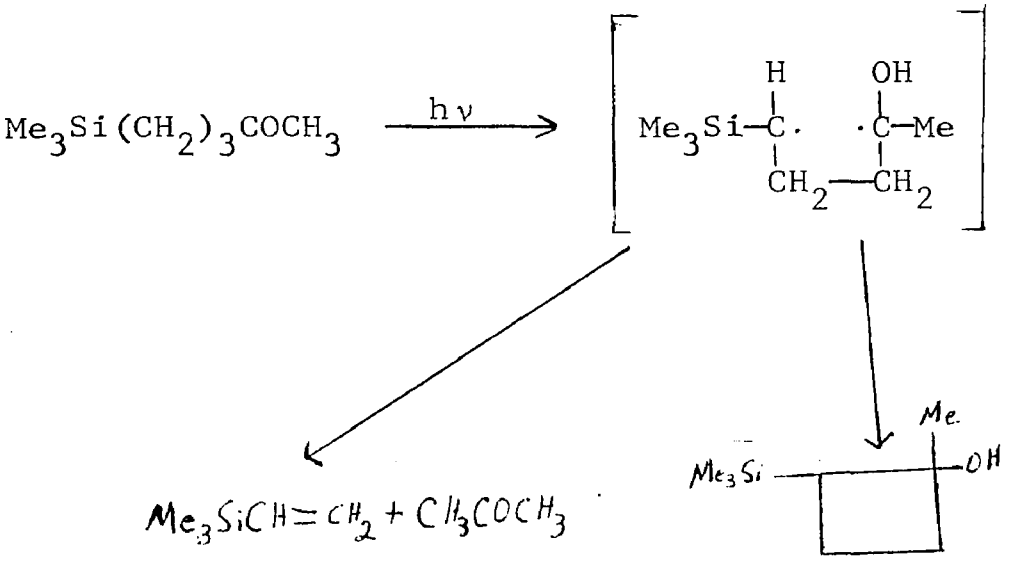
[a]The vinyltrimethylsilane was lost by evaporation.

[b]The percentage is by weight.



(45)

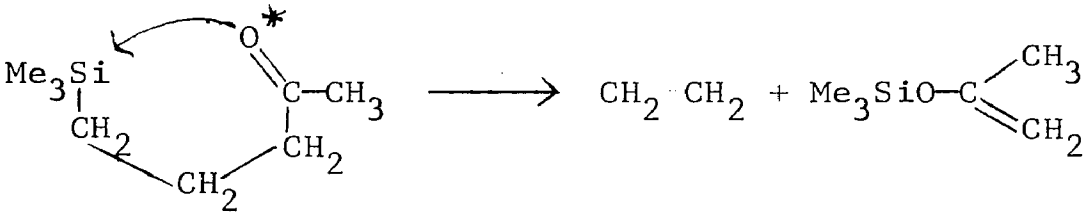
Compound V reacts very similarly to the straight chain compounds photolysed by Yang and Yang.[10] According to their suggested mechanism, the following reaction routes can be written:



(46)

An important pathway in this case is the cleavage to give vinyltrimethylsilane according to the Norrish Type II reaction. The acetone would be expected as another product. It would photolyse rapidly under the reaction conditions. The gas-

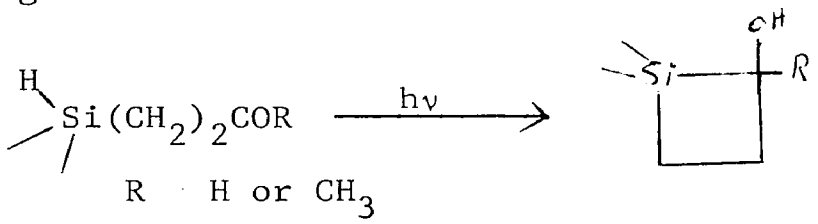
liquid chromatogram using the Apiezon L column gave a small peak with the same retention time as that of acetone. This was only 1-2% of the reaction product mixture. The yields of the cyclobutanol are similar to those obtained by Yang and Yang[10] and by Orbin.[11] There was no evidence from the major products that there was any attack of the excited oxygen in the carbonyl on the silicon atom as in equation (47). This would give products containing the silicon-oxygen bond. None was detected by infrared spectroscopy.



(47)

D. 1-Sila-1-phenyl-4-butanal (XVII)

Considering the formation of cyclobutanols from several different ketones which have been photolysed in solution (Eq. (29), (31), and (46)), it should be of interest to determine what the reaction would be if the necessary γ-hydrogen were on the silicon atom.

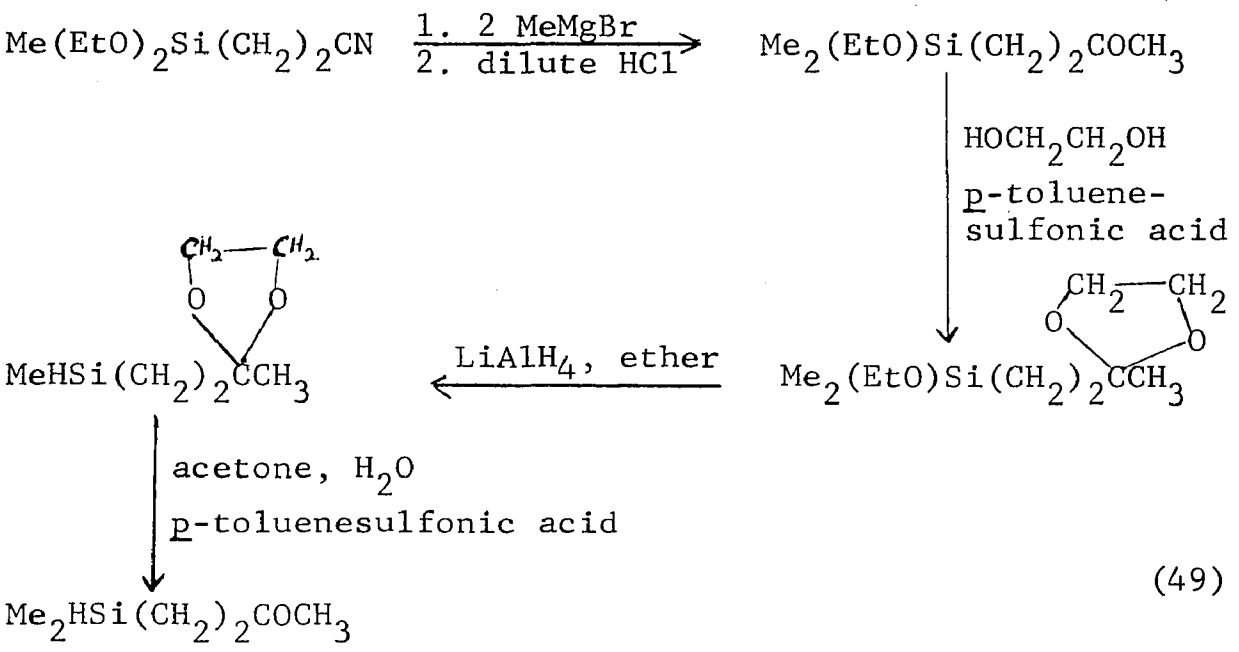


R H or CH_3

(48)

Several attempts were made to produce this type of ketone in good yield. Some of these will be mentioned briefly.

One of the first attempts was the β-cyanoethyl-methyldiethoxysilane (a gift from General Electric). The following sequence of reactions was attempted:



(49)

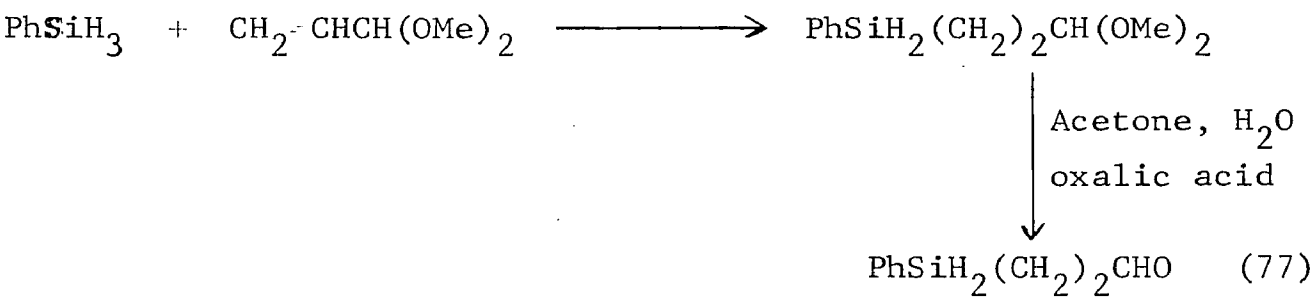
All the steps were followed by infrared spectroscopy. The indication was that all of the steps went except the last one, which gave primarily polymer. The silicon-hydrogen bond is stable in a pure compound, but acids and bases easily cleave it.

In another attempt the product obtained from a reaction of methyldichlorosilane, vinyl methyl ketone and platinum on charcoal for 24 hrs. under reflux was treated with tributyltin hydride and triphenyltin hydride. The conditions were varied from mixing at room temperature to heating on a water bath for 7 hrs. An infrared spectrum of the distillate indicated the presence of the carbonyl group, but the silicon-hydrogen band was very weak. Even catalytic amounts of 2,2'-azobis(2-methylpropionitrile) did not give the desired silane.

In other attempts pentylsilane and phenylsilane were heated with vinyl methyl ketone in a bomb at 200-250° and 500 p.s.i. for 30 hours using platinum on charcoal as the catalyst. In every case the major product was undistillable

polymers.

The most productive method was by the hydrolysis of the addition product of phenylsilane and 3,3-dimethoxypropene-2 in the presence of t-butyl peroxybenzoate.



(77)

There was good evidence that the aldehyde had formed but the difficulty arose in the separation from the remaining acetal. The infrared spectrum (see the Experimental section) of the product mixture contained strong silicon-hydrogen and carbonyl bands. The ether band of the acetal was also present. Distillation gave a fluffy, white foam rubber. Elution through a silica column with pentane caused decomposition as considerable gas formed within the column. The best separation was achieved using a pure glucose column and eluting with pentane. However, the acetal group was still present. As the acetal was stable to ultraviolet light, some of the mixture was photolysed in cyclohexane according to procedure (b). The aldehyde reacted to about 60-67% in 25 hrs. of photolysis. There was no formation of gas. There was no formation of alcohol as detected from the infrared spectrum. This is enough to show that cyclization does not occur with this compound to form a cyclobutanol. Aldehyde XVII seems to be stable when pure with the acetal but when some was dissolved in carbon tetrachloride for an NMR spectrum, gas slowly evolved and when the solvent was evaporated a few hours later, only a colorless rubber remained.

E. 2-Sila-2,2-dimethyl-5-phenylpentan-5-one (VI)

Moving next to the compounds which contain two methylene carbons between the carbonyl and silicon atom, 2-sila-2,2-dimethyl-5-phenylpentan-5-one is the phenyl ketone, $Me_3Si(CH_2)_3COPh$. This compound was prepared by two methods. The first was by the addition of benzaldehyde to trimethylvinylsilane in the presence of benzoyl peroxide as the catalyst. This work is similar to that of Petrov and co-workers[17] who added both aromatic and aliphatic aldehydes to vinylsilanes.

$$Et_3SiCH{=}CH_2 + PhCHO \xrightarrow{Bz_2O_2} Et_3Si(CH_2)_2COPh \qquad (50)$$

$$Et_3SiCH{=}CH_2 + C_3H_7CHO \xrightarrow{\quad " \quad} Et_3Si(CH_2)_2COC_3H_7 \qquad (51)$$

Sommer[18] added aliphatic aldehydes to vinyltrimethylsilane.

$$Me_3SiCH{=}CH_2 + C_3H_7CHO \xrightarrow{Ac_2O_2} Me_3Si(CH_2)_2COC_3H_7 \qquad (52)$$

It proved difficult to remove all of the benzaldehyde from the reaction by distillation. However, the aldehyde easily oxidized in the air to benzoic acid which remained behind upon distillation.

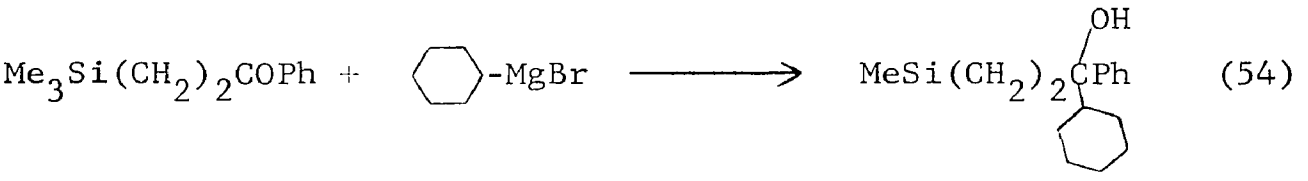
The second method of preparing 2-sila-2,2-dimethyl-5-phenylpentan-5-one was by treating the nitrile with phenylmagnesium bromide according to the method of Petrov and Vdovin.[19]

$$Cl_3Si(CH_2)_2CN + 3MeMgBr \longrightarrow Me_3Si(CH_2)_2CN$$

$$\xrightarrow[2.\ HCl,\ H_2O]{1.\ PhMgBr} Me_3Si(CH_2)_2COPh \qquad (53)$$

The silicon was methylated with minimum effect on the nitrile by adding the Grignard reagent to the nitrile solution and hydrolyzing immediately. The imine which was formed upon hydrolysis of the Grignard complex was destroyed immediately by the addition of hydrochloric acid to the solution. This ketone was identical with the ketone prepared from benzaldehyde and trimethylvinylsilane in both infrared spectrum and photochemical reactions.

2-Sila-2,2-dimethyl-5-phenylpentan-5-one was photolysed according to procedures (a) and (b). The conditions of the photolyses and distribution of the products are given in Table VI. The major product identified in run No. 1 was 2-sila-2,2-dimethyl-5-cyclohexyl-5-phenylpentan-5-ol in a 10% yield. This yield was estimated by conversion to the 3,5-dinitrobenzoate ester which was purified by chromatography on a silica column. This alcohol had an infrared spectrum identical with that of the authentic alcohol prepared by adding cyclohexylmagnesium bromide to the starting ketone.



(54)

Another product, isolated in 6% yield, was 2-sila-2,2-dimethyl-4-cyclohexylbutane, $Me_3Si(CH_2)_2-\bigcirc$. Its identity was shown, after isolation by gas-liquid chromatography, by comparison of its infrared spectrum with that of an authentic sample. The remainder of the product was a heavy oil. The infrared spectrum of this oil had bands at 3420 (s), 3040 (w) 2920 (s), 2850 (m), 1690 (s), 1490 (m), 1450 (m), 1246 (s), 1175 (m), 1065 (s), 1025 (m), 860 (s), 830 (s), 765 (m), and 695 (m) cm^{-1} indicating the presence of alcohol, ketone, and trimethylsilyl groups. By gas-liquid

TABLE VI

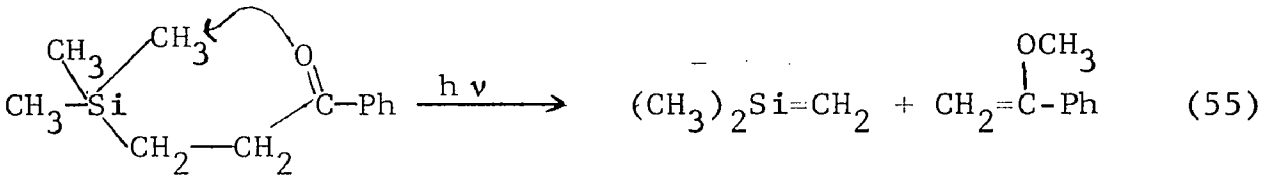
Photolysis of 2-sila-2,2-dimethyl-5-phenylpentan-5-one

No.	Solvent[a]	Time (hrs.)	Percent reacted	Conditions
1	91% cyclohexane	8	35	(a) Vycor Filter
2	91% cyclohexane	16	80	(a) Vycor Filter
3	37% methylcyclohexane	72	43	(b) no filter
4	60% methylcyclohexane	72	21	(b) no filter
5	70% ethanol	50	5-10	(b) no filter

[a]Percentage is by weight.

chromatography trace amounts of vinyltrimethylsilane and 1, 4-bis(trimethylsilyl)butane were also detected. These were present, however, in no more than 1-2% yields. There was some evidence, based only on the retention time, of trace amounts of biphenyl.

Considering the products which were formed, it is not surprising that the molecule resists cleavage. This property is also common to carbon compounds without hydrogens gamma to the carbonyl. From the products there was no evidence for the possible reaction suggested in the Statement of Problem, Eq. (36), where the activated oxygen would attack the silicon atom which has no γ-hydrogens removing a methyl group gamma to the carbonyl.



(55)

F. 2-Sila-2,2-dimethylhexan-5-one (VII)

The methyl ketone corresponding to compound VI is 2-sila-2,2-dimethylhexan-5-one, $Me_3Si(CH_2)_2COCH_3$. This compound was prepared according to Petrov and co-workers[20] by treating the nitrile with methylmagnesium bromide and hydrolyzing with hydrochloric acid to decompose the imine.

$$Cl_3Si(CH_2)_2CN + 4\ MeMgBr \xrightarrow[2.\ HCl,\ H_2O]{} Me_3Si(CH_2)_2COCH_3 \qquad (56)$$

Both procedures (a) and (b) were used in the photochemical reactions. The results can be found in Table VII. In each of these reactions there was a large amount of polymeric material ranging from 20-30% of the weight of the reacted ketone. This accounts for most of the starting ketone.

TABLE VII

Photolysis of 2-sila-2,2-dimethylhexan-5-one

Conditions

No.	Solvent[b]	Time (hrs.)	Percent reacted	Procedure and Filter
1	94% cyclohexane	4	60-70	(a) Vycor
2	30% cyclohexane	49	85	(b) no filter
3	30% cyclohexane	56	85	(b) no filter
4	30% ethanol	50	95	(b) no filter

Percent yield

No.	$Me_3SiCH_2CH_3$	$Me_3SiCH{=}CH_2$	$CH_3COCOCH_3$	$(Me_3SiCH_2CH_2)_2$
1	-	Lost[a]	13	60
2	14	33	8	36
3	17	39[c]	12	31
4	17	39	15	29

[a]Most of the vinyltrimethylsilane was lost in the nitrogen bubbled through the reaction vessel.

[b]Percentages by weight.

[c]The total yield for vinyltrimethylsilane and ethyltrimethylsilane was 56%.

No gas was detected in this reaction or in any of the other reactions of silicon compounds. The yields were determined by gas-liquid chromatography. The yield of 1,4-bis(trimethylsilyl)butane in run No. 1 is in question as the accuracy of the early yield-determinations was not very good.

The nature of the products indicates that one of the major routes in this reaction is the cleavage of the bond between the carbonyl carbon and the silicon-containing chain. The acetyl radicals produce 2,3-butanedione by coupling, which then reacts further to form other products.

$$Me_3Si(CH_2)_2COCH_3 \xrightarrow{h\nu} Me_3SiCH_2CH_2\cdot + CH_3CO\cdot \quad (57)$$

$$2\ CH_3CO\cdot \longrightarrow CH_3COCOCH_3 \quad (58)$$

$$2\ Me_3SiCH_2CH_2\cdot \longrightarrow (Me_3SiCH_2CH_2)_2 \quad (59)$$

$$Me_3SiCH_2CH_2\cdot + R\cdot \longrightarrow Me_3SiCH{=}CH_2 + RH \quad (60)$$

This reaction is not surprising. It resembles the photolysis of acetone and some other ketones which do not have any hydogens gamma to the carbonyl. Methyl ketones, apparently, cleave more easily to give the acetyl radical than do phenyl ketones to give the benzoyl radical. This is evidenced in the much higher reactivity of acetone over acetophenone in photolyses.

There is also the possibility that the trimethylsilylethyl radical would abstract hydrogen from other radicals or molecules to form ethyltrimethylsilane, Eq. (61).

$$RH + Me_3SiCH_2CH_2\cdot \longrightarrow R\cdot + Me_3SiCH_2CH_3 \quad (61)$$

There were two pieces of evidence for the presence of ethyltrimethylsilane. First, on the Apiezon L column the latter appears as a shoulder on the vinyltrimethylsilane peak. This same shoulder was present in the photolysis product to the

extent of about 30-35% of the total peak, and it had the same retention time as ethyltrimethylsilane. Secondly, the vinyl bands at 960 and 1006 cm^{-1} in the infrared spectrum of the mixture were weaker relative to the trimethylsilyl band at 1245 cm^{-1} than in an infrared spectrum of pure vinyltrimethylsilane. This would indicate that the 56% yield reported for vinyltrimethylsilane in Table VII would actually be 39% vinyltrimethylsilane and 17% ethyltrimethylsilane.

G. Trimethylsilylacetophenone (VIII)

The phenyl ketone with only one methylene carbon between the silicon atom and the carbonyl is trimethylsilylacetophenone, Me_3SiCH_2COPh. This compound was made by reaction of the Grignard reagent of chloromethyltrimethylsilane with benzoic anhydride at -60°.

$$Me_3SiCH_2MgCl + (PhCO)_2O \longrightarrow Me_3SiCH_2COPh \qquad (62)$$

Precautions must be taken with this compound because it hydrolyzes quite easily, even in the presence of moisture in the atmosphere, to hexamethyldisiloxane and acetophenone. When some of the trimethylacetophenone was eluted through alumina with pentane and ether, nothing but acetophenone was recovered. Elution through silica with dry pentane gave about a fifty-fifty mixture of the silane and acetophenone. The ketone also solvolyzed easily with absolute ethanol giving trimethylethoxysilane and acetophenone.

Because of the sensitivity of this compound to hydrolysis, it was necessary to take the proper precautions in the photolysis work. The solvents were dried over sodium, and the apparatus was dried in an oven at 100°. During the preparation of the samples, contact with the atmosphere was minimized. The ketone was purified by gas-liquid chromatography just

before photolysis. The quartz tubes were sealed after flushing with argon. In the work in which rubber policemen were used, the products, hexamethyldisiloxane and acetophenone, were obtained in large yields. The results are given in Table VIII

TABLE VIII

Photolysis of Trimethylsilylacetophenone

No.	Solvent	Time (hrs.)	Percent reacted	Yield $(Me_3Si)_2O$
1	61% methylcyclohexane	90	1-3%	trace [a]
2	62% "	68	14	24 [b]

a. This run was photolysed with an older lamp.

b. This yield, as were all others, was based on the amount of ketone reacted.

This ketone is even more stable to ultraviolet light than those previously discussed. It is not certain if the small amount of hexamethyldisiloxane produced originates from traces of water in the system. Of the total reaction system, the disiloxane is present to the extent of only 3.6% in run No. 2. The weight of the total reaction mixture was only about 200-300 mg. Therefore, there would be only 5-7 mg. of hexamethyldisiloxane present. Consideration of the stoichiometry of the hydrolysis of trimethylsilylacetophenone, 0.18 gram of water will produce 1.6 gram of hexamethyldisiloxane. The ratio is almost ten to one. Therefore, 0.5-1 mg. of water in the system could give a yield of 24% hexamethyldisiloxane. When moisture was carefully excluded (runs 1 and 2 in Table VIII), no acetophenone was obtained. On the other

hand, these photolyses were compared with blanks made by sealing a sample of the reaction solution in a capillary tube for comparison with photolysis products. In no case had hexamethyldisiloxane formed in the unphotolysed sample. This could, at least, indicate that the ultraviolet light was responsible for the formation of the hexamethyldisiloxane regardless of where the oxygen originated.

If this reaction were to produce trimethylsilyl and benzoyl radicals, then the presence of hexamethyldisilane might be expected. However, the disilane was not detected. An experiment was carried out to determine the reactivity of hexamethyldisilane in the presence of the ultraviolet light. When it was photolysed in the presence of acetone with moisture present, the acetone and disilane both reacted readily, giving several higher molecular weight compounds and hexamethyldisiloxane in an 18% yield. However, when the acetone was dry, the hexamethyldisilane was quite unreactive under the conditions of procedure (b). Also, hexamethyldisilane did not photolyse in the presence of acetophenone.

An experiment was conducted to determine if ultraviolet light would catalyze the solvolysis of trimethylsilylacetophenone. A mixture of this ketone (0.0020 mole), water (0.002 mole), and ethyl ether (60% of total weight) was divided into two parts. One was photolysed in sealed quartz tubes for 7.5 hrs. according to procedure (b). The other portion was sealed in Pyrex tubes and protected from the irradiation in the same bath with aluminum foil. Analysis by gas-liquid chromatography indicated that the unphotolysed sample had solvolyzed to the extent of 20% during this period giving trimethylsilanol and acetophenone. In the photolysed sample, the starting ketone had almost completely reacted, giving a 95-100% yield of trimethylsilanol. The acetophenone had almost completely photolysed (5-10% yield). This is good

indication that the rate of solvolysis of trimethylsilylacetophenone is increased by ultraviolet light. This is probably the major reaction with adventitious traces of water which occurred when the ketone was photolysed under ostensibly anhydrous conditions. Further photolysis of the above mixture indicated that the trimethylsilanol was converting slowly to hexamethylsiloxane. This was also true for the unphotolysed mixture. This accounts for the hexamethylsiloxane obtained after the lengthy photolyses reported earlier.

Concerning the absence of acetophenone in the above experiment, it would be of interest to determine how it would photolyse under these conditions. A solution of acetophenone (0.0017 mole) and water (0.0014 mole) in dry ether (70% of total weight) was photolysed under the same conditions. Ninety-five percent of the acetophenone reacted during the eight hours of photolysis. Therefore, acetophenone would not be expected to go unreacted in the former experiment.

H. Trimethylsilylacetone (IX)

The simplest methyl ketone studied was trimethylsilylacetone, $Me_3SiCH_2COCH_3$. This compound was prepared according to the procedure of Hauser and Hance.[21]

$$Me_3SiCH_2MgCl + (CH_3CO)_2O \xrightarrow{-70°} Me_3SiCH_2COCH_3 \qquad (63)$$

In this reaction, acetone and hexamethyldisiloxane were also formed. It was difficult to remove all of these impurities. When purification of this ketone on a 20 foot silicone nitrile column was attempted, decomposition occurred. Precautions were also needed to protect the ketone from moisture. Absolute ethanol slowly solvolyzed the ketone in the hexamethyldisiloxane impurity forming ethoxytrimethylsilane and acetone. The

ketone had reacted to the extent of about 50% in two days.

The ketone was photolysed according to procedures (b) and (c). One sample was photolysed for 70 hrs., according to procedure (b), in cyclohexane which had been dried with sodium with very little reaction. In this case, the ketone had been purified by gas-liquid chromatography using the silicone oil 200 column. When the ketone was photolysed in the presence of the impurities, hexamethyldisiloxane and acetone, it reacted more rapidly giving hexamethyldisiloxane. It is difficult to say if the acetone was the other product as the acetone in the system photolysed as fast as, or faster than, trimethylsilylacetone. There is, no doubt, water present in the system from the coupling of small quantities of trimethylsilanol which was shown to be a major product from the original preparation.

$$2\ Me_3SiOH \longrightarrow (Me_3Si)_2O + H_2O \qquad (64)$$

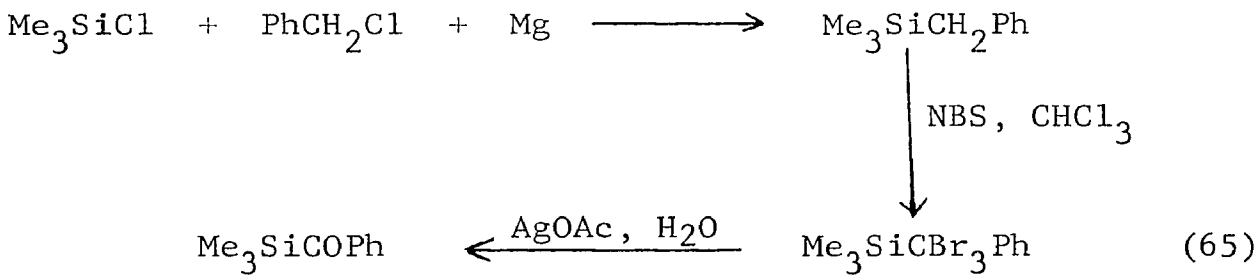
With this ketone also, there is the possibility of photocatalytic solvolysis. In order to test this, a mixture of trimethylsilylacetone (0.0004 mole), water (0.0003 mole), and anhydrous ethyl ether (60% of total weight) was photolysed for 21 hrs. and analyzed as described for trimethylsilylacetophenone. The analysis indicated that the unphotolysed control sample was mostly unreacted, whereas the photolysed part had reacted to the extent of 60-70%. Trimethylsilanol was obtained in a 100% yield. This clearly shows that hydrolysis of trimethylsilylacetone in ether is photocatalyzed. The trimethylsilanol slowly reacts to give hexamethylsiloxane and water as shown in Eq. (64). The photolysis of trimethylsilylacetone (10% of total weight) in ethanol (with 0.05% water) for 70 hrs., according to procedure (b), gave 80% hexa-

methyldisiloxane and only a small quantity (10-15%) of ethoxytrimethylsilane. However, when the same ketone was solvolyzed without irradiation in the same solvent, ethoxytrimethylsilane was the major product. It should be remembered that ethoxytrimethylsilane will itself hydrolyze to hexamethyldisiloxane.

Because acetone was obtained only in trace quantities in the photolysis of trimethylsilylacetone with water, it would be of interest to determine how acetone would photolyse under these same conditions. A solution of acetone (0.027 mole) and water (0.002 mole) in dry ether (65% of the total weight) was photolysed for eight hours under the same conditions. Ninety to ninety-five percent of the ketone reacted during this time. According to this experiment, acetone would not be expected to go unreacted in the photolysis of trimethylsilylacetone in water.

I. Benzoyltrimethylsilane (X)

The last ketone containing a silicon atom to be photolysed was benzoyltrimethylsilane, $Me_3SiCOPh$. This compound was first prepared by Brook and co-workers.[22] The same sequence of steps was used in this laboratory except for the preparation of benzyltrimethylsilane.



(65)

The Barbier reaction as a method of producing benzyltrimethylsilane went very smoothly and much quicker than a Wurtz-Fittig reaction which had been tried earlier. The ketone is a bright yellow liquid which slowly hydrolyzes in the presence of

moisture. The ketone did not readily solvolyze in the presence of absolute ethanol, but a slow solvolysis rate has been detected giving ethoxytrimethylsilane and hexamethyldisiloxane after 3-4 weeks. The latter was obtained in the larger quantity.

Because of the sensitivity to moisture, special precautions had to be taken in the photolysis of the ketone. The apparatus was oven-dried and the hydrocarbon solvents were dried with sodium. The ethanol was dried with magnesium as described by Vogel.[23] The ketone was photolysed according to procedures (b) and (c). Table IX gives the data of several reactions. All experiments listed in the table were according to procedure (b). Only a few runs were degassed according to procedure (c). In these runs the yield of hexamethyldisiloxane was so small that it was not even calculated. One difficulty in the photolysis of benzoyltrimethylsilane was the formation of a deposit on the walls of the tube. This was to a much greater extent than for any other reaction. The deposit was a dark,red-brown material which absorbed the ultraviolet light. The solid was more common in the runs containing no alcohol than in those with alcohol.

The remainder of the product was examined for the possible presence of other identifiable compounds. Investigation by thin layer chromatography indicated that, besides the spots for the starting ketone and benzaldehyde, two other spots moved from the original position. One small one with the solvent of benzene, cyclohexane, and chloroform (5:3:1 in volume) had an R_f value of 1. The other spot of considerable size had a R_f value of 0.16. This spot and some material which did not move on the plate were separated by column chromatography using a silica column with gradual change of

TABLE IX

Photolysis of benzoyltrimethylsilane

No.	Solvent[a]	Time (hrs.)	Percent reacted	Percent yields Me_3SiOEt	Percent yields $(Me_3Si)_2O$	Percent yields PhCHO
1	28% ethanol 33% methylcyclohexane	55	100	5	92	9
2	53% methylcyclohexane	68	31	0	19	15
3	neat	68	29	0	18	24
4	35% ethanol 28% methylcyclohexane	55	100	7	103	9
5	50% ether 7% methylcyclohexane	55	21	0	17	12
6	50% ethyl acetate 12% methylcyclohexane	55	15	0	19	18
7	39% t-butyl alcohol 29% methylcyclohexane	55	100	0	71	7
8	2% ethanol 41% methylcyclohexane	53	30	15[b] 65[c]	41	20
9	8% t-butyl alcohol 26% methylcyclohexane	53	45	0	20	15
10	42% methylcyclohexane	53	38	0	30	12

[a]Percentages by weight; remainder was the ketone

continued - p. 35

TABLE IX continued

No.	Solvent	Time (hrs.)	Percent reacted	Percent yields		
				Me_3SiOEt	$(Me_3Si)_2O$	PhCHO
11[d]	61% ethanol	22.8	95-100	trace	88	trace
12[d]	61% ethanol	22.8	95-100	trace	93	trace

[b]Yield based on the ketone reacted.

[c]Yield based on the ethanol reacted.

[d]The mixture contained water (0.00115 mole) with 0.0028 mole of the ketone.

solvent from pentane to ether. These products are responsible for most of the weight of the photolysed ketone. Molecular weight determinations by osmometer indicated that three of these fractions had molecular weights of 265, 600, and 632. The infrared spectrum of the second fraction contained bands at 2000 (m), 2900 (m), 1685 (s), 1600 (m), 1500 (m), 1450 (m), 1275 (s), 1175 (m), 1100 (m), 1025 (m), 840 (m), 750 (m), and 700 (s) cm^{-1}. Analysis of this fraction gave 79.70% carbon and 5.54% hydrogen with no residue. This would correspond to an empirical formula of $C_{6.6}H_{5.5}O$. This agrees with the infrared spectrum in that no silicon was present. The spectra of all the fractions were similar except that in the first fraction there was a strong band at 925 cm^{-1}. Sublimation of this fraction gave 20-30% benzoic acid which was responsible for this band. The molecular weight of the yellow material after removal of the benzoic acid was 538. Therefore, the major products from the photolysis of benzoyltrimethylsilane are higher molecular weight materials.

A major problem in this reaction concerns the oxygen. The source of the oxygen in the hexamethyldisiloxane produced in runs containing only hydrocarbon solvents is not obvious. It could come from traces of oxygen or moisture. As pointed out in the discussion for compound VIII, approximately one milligram of water could give a substantial amount of the disiloxane. In all cases control samples of the material to be photolysed were sealed in capillary tubes for comparison in gas-liquid chromatography. In no case was there any of the disiloxane produced in the unphotolysed samples during the two to three days before analysis. In reactions where ethanol was present, 0.53-0.64 mole of the ethanol reacted per mole of benzoyltrimethylsilane in the several runs

examined. This is quite constant whether the ethanol was present in limited amounts or in excess. These observations indicate that the photolysis speeds up the solvolysis of the ketone.

To determine if this is a catalyzed solvolysis reaction, an experiment was run in which benzoyltrimethylsilane was photolysed in the presence of water (2 to 1 mole rate) in ethanol solution. The reaction mixture was divided into two parts, one in sealed quartz tubes for photolysis and one in sealed glass tubes for comparison. Both tubes were placed in the same bath according to procedure (b). The control sample was wrapped with aluminum foil to prevent exposure to the ultraviolet light. In the control sample no hydrolysis products were detectable after 23 hrs. In the same time the photolysed mixture had reacted completely giving 85-95% hexamethyldisiloxane with a trace of ethoxytrimethylsilane. This shows that the solvolysis is catalyzed by the irradiation. No benzaldehyde was recovered.

In a controlled experiment, a mixture of benzaldehyde (0.0020 mole) and water (0.0017 mole) in dry ether (65% of the total weight) was photolysed for 8 hrs. The aldehyde reacted completely. Therefore, benzaldehyde would not be expected to go unreacted in the former experiment.

J. 4-(1-Phenyl-1-oxobutyl)trimethyltin (XI)

Now turning to the tin compounds, the first one to be photolysed was 4-(1-phenyl-1-oxobutyl)trimethyltin, $Me_3Sn(CH_2)_3COPh$. The ketone was prepared by way of the nitrile.

$$Me_3SnH + CH_2{=}CHCH_2CN \xrightarrow{AIBN} Me_3Sn(CH_2)_3CN$$

$$\downarrow \text{ 1. PhMgBr; 2. } H_2O, \text{ heat}$$

$$Me_3Sn(CH_2)_3COPh \qquad (66)$$

Upon treating the nitrile with phenyl Grignard reagent the imine was formed. This was hydrolyzed by heating with water according to the procedure of Noltes and vander Kerk.[24] Because of the high boiling point of this ketone, purification was effected by eluting through a column of silica using pentane as the eluent. Purity was checked by thin layer chromatography.

This ketone was photolysed according to procedures (b) and (c). Because gases were evolved, balloons were placed on the tubes in procedure (b). In procedure (c), a gas buret was used to measure the quantity of gas produced. The results are given in Table X. It was assumed that all of the gas evolved was methane although the infrared spectrum of the gas indicated that traces of ethane were present. The acetophenone and vinyltrimethyltin were determined by gas-liquid chromatography using the silicone oil 200 column. The yield of dimethyltin oxide was determined by dissolving the washed precipitate which formed upon exposing the reaction mixture to the atmosphere in 18% hydrochloric acid and weighing the brown residue which remained after drying. This amounted to 15-25% of the weight of the precipitate, depending on the ketone. By eluting the photolysed mixture through a silica column with pentane small quantities of 1,2-dibenzoylethane and 2,3-diphenylbutane-2,3-diol were obtained. Each of these was present in 10-15% yields.

TABLE X

Photolysis of 4-(1-phenyl-1-oxobutyl)trimethyltin

No.	Solvent[a]	Time (hrs.)	Percent reacted	Conditions	$(Me_2SnO)_x$	CH_4	$PhCOCH_3$	$Me_3CH=CH_2$
1	24% n-hexane	11.5	95-100	(b)	-	-	58	30
2	22% n-hexane	6.5	95-100	(b)	-	-	58	24
3	neat	9.3	90-100	(b)	-	-	55	15
4	73% methyl-cyclohexane	9.4	85	(c) degassed	-	34	30	-
5	74% methyl-cyclohexane	9.4	85	(c) degassed	-	31	39	-
6	75% octane	5.3	90	(c) degassed	15	36	36	0
7	75% octane	5.3	90	(c) not degassed flushed with argon	16	33	34	0
8	75% ethanol	8.0	90	(c) not degassed flushed with argon	5.2	31	25	16
9	67% n-hexane	8.0	80	(c) not degassed in Pyrex tube flushed with argon	16	25	45	17
10	80% cyclohexane	8.5	95	(c) degassed sulfur added	0	31	-	0

continued - p. 40

TABLE X continued

No.	Solvent[a]	Time (hrs.)	Percent reacted	Conditions	$(Me_2SnO)_x$	CH_4	$PhCOCH_3$	$Me_3CH{=}CH_2$
11	80% cyclohexane	8.5	95	(c) degassed iodine added	0	35	-	-
12	35% chloro-cyclohexane 55% methyl-cyclohexane	8.0	95-100	(c) degassed	11	34	20	0
13	35% bromo-cyclohexane 55% methyl-cyclohexane	8.0	95-100	(c) degassed	5	32	-	0

[a]Percentage is by weight; remainder was ketone.

Considerable investigation was done on the dimethyltin oxide. First, some of the oxide was dissolved in 18% hydrochloric acid and then the acid and water were removed under vacuum. The white crystals were dissolved in water and a solution of ammonium salicylate was added. An immediate white precipitate of fine crystals was formed. After drying they melted at 298-302° and gave an infrared spectrum identical with that of dimethyltin salicylate which was made from dimethyltin dichloride and ammonium salicylate.[26] It is conceivable that the dimethyltin oxide was formed from dimethyltin and oxygen from the atmosphere. This is suggested by the fact that little precipitate forms in the tubes which are degassed until they are opened to the atmosphere. If dimethyltin is present it should react with sulfur and iodine readily. No precipitate was formed in run No. 10 when a solution of sulfur in toluene was added immediately upon opening the tube. Elution through a column of silica with pentane gave some impure crystals which gave a spectrum identical to that of dimethyltin sulfide prepared from dimethyltin dichloride and sodium sulfide. Similarly, when a solution of iodine in ether was added to the photolysed material, no oxide was formed. The diiodide was extracted with water and precipitated as the salicylate with ammonium salicylate. An overall yield of 10% was obtained. Theoretically it should be 16% as with the oxide, but this would assume that the reactions were quantitative.

K. 5-(2-Oxopentyl)trimethyltin (XII)

The production of 5-(2-oxopentyl)trimethyltin, $Me_3Sn(CH_2)_3COCH_3$, was very similar to that used in preparing the other tin compounds discussed. The addition products from trimethyltin hydride and allyl cyanide were treated with methyl-

magnesium bromide to give the imine. This was then hydrolyzed by heating with water.

$$Me_3SnH + CH_2{=}CHCH_2CN \xrightarrow{AIBN} Me_3Sn(CH_2)_3CN$$

$$\downarrow \text{1. MeMgBr; 2. } H_2O, \text{ heat}$$

$$Me_3Sn(CH_2)_3COCH_3 \qquad (67)$$

Even after distillation, thin layer chromatography indicated the presence of an impurity which was removed by eluting through a silica column with pentane.

This ketone was photolysed according to both procedures (b), in Pyrex tubes, and (c). The work according to procedure (b) was only qualitative and the products identified were methane, dimethyltin oxide (the rubber balloons used for sealing the tubes did not exclude the oxygen well), and vinyltrimethyltin in 6% yield. Table XI gives the results and yields obtained according to procedure (c). No vinyltrimethyltin was obtained in the samples which were photolysed in quartz tubes.

TABLE XI

Photolysis of 5-(2-oxopentyl)trimethyltin

No.	Solvent	Time (hrs.)	Percent reacted	Percent yield $(Me_2SnO)_x$	Percent yield CH_4
1	84% cyclohexane	34	30%	42%	67%
2	85% "	36	31	40	71

The solvent, cyclohexane, was dried over sodium before use. The volume of the gas evolved was determined by the gas buret. The infrared spectrum of the gas contained a small band at 2200 cm^{-1}. This characteristic band for carbon monoxide indicated that the gas was present to an extent of 1-4% of the volume. There were also small bands characteristic of ethane present in the infrared spectrum.

The presence of vinyltrimethyltin in some of the reactions indicated that the Norrish Type II mechanism may have occurred to a small extent giving a lower molecular weight ketone and olefin. The other product, acetone, would have reacted further under these conditions. The major reaction gave dimethyltin which reacted upon exposure to the atmosphere forming dimethyltin oxide.

L. 3-(1-phenyl-1-oxopropyl)trimethyltin (XIII)

3-(1-phenyl-1-oxopropyl)trimethyltin, $Me_3Sn(CH_2)_2COPh$, was prepared by adding trimethyltin hydride to acrylonitrile in the presence of 2,2'-azobis(2-methylpropionitrile) as the catalyst. The nitrile was treated with phenylmagnesium bromide, and the imine formed was decomposed by heating with water.

$$Me_3SnH + CH_2{=}CHCN \xrightarrow{AIBN} Me_3Sn(CH_2)_2CN \xrightarrow[2.\ H_2O,\ heat]{1.\ PhMgBr} Me_3Sn(CH_2)_2COPh \qquad (68)$$

Because the ketone tends to decompose upon distillation, purification was performed by eluting with pentane through a silica column. The purity was checked with thin layer chromatography.

Photolysis of this ketone was done according to procedures (b) and (c). The quantitative work was performed according to the latter procedure. The results of the photolyses are given in Table XII. In both cases the photolyses were done in quartz tubes, and the solutions were degassed according to the procedure. The solvent was cyclohexane in the two reported cases.

TABLE XII

Photolysis of 3-(1-phenyl-1-oxopropyl)trimethyltin

No.	Solvent	Time (hrs.)	Percent reacted	Percent yield $(Me_2SnO)_x$	Percent yield CH_4
1	81%	21	65%	21%	39%
2	82	21	65	23	41

Because the ketone decomposes on the gas-liquid chromatography columns, the percent reacted was estimated by the size of the spot on the thin layer chromatographic plate. The same procedures were used as before in determining the products.

This ketone reacted in a manner similar to the other tin compounds photolysed. The main difference was that this reaction produced more red-yellow gum as the product. Upon photolysis of samples where only 20-30% hydrocarbon solvent was present the mixture would turn to a clear, red gel. Similar quantities of absolute ethanol would give a colorless gel. When ether or acetone was used to wash this red gel from the photolysis tube the dimethyl tin oxide would form immediately upon solution. Yet, there remained a considerable amount of a red-yellow gum when the filtered solution had evaporated.

Some of this material was eluted through a neutral alumina column with gradual increase in the polarity of the solvent to acetone. A yellow gum was recovered from the column. It gave a molecular weightof 501 (in toluene) in the osmometer. The infrared spectrum of this material gave bands at 3400 (s), 3050 (w), 2980 (s), 2925 (m), 1950 (s), 1820 (s), 1690 (s), 1610 (s), 1590 (m), 1500 (s), 1460 (s), 1375 (m), 1255 (m), 1225 (s), 1180 (m), 1165 (w), 1070 (m), 1005 (s), 980 (s), 960 (m), 920 (m), 845 (m), 760 (s), and 700 (s) cm^{-1}.

This very complicated spectrum was not much different from a spectrum of the photolysis mixture before elution. Outside of the methane and dimethyltin oxide which is also a polymer, all of the ketone forms polymer in the photolysis reaction.

M. 4-(2-Oxobutyl)trimethyltin (XIV)

The last tin compound to be photolysed was 4-(2-oxobutyl)trimethyltin, $Me_3Sn(CH_2)_2COCH_3$. The preparation of this ketone was very similar to the previous tin compounds. The following sequence of reactions show the steps:

$$Me_3SnH + CH_2{=}CHCN \xrightarrow{AIBN} Me_3Sn(CH_2)_2CN$$

$$Me_3Sn(CH_2)_2CN \xrightarrow[2.\ H_2O,\ heat]{1.\ MeMgBr} Me_3Sn(CH_2)_2COCH_3 \qquad (69)$$

Thin layer chromatography indicated that the distilled ketone was quite pure. Upon standing in the atmosphere for some time, some white precipitate formed. Therefore, the compound was stored in sealed tubes.

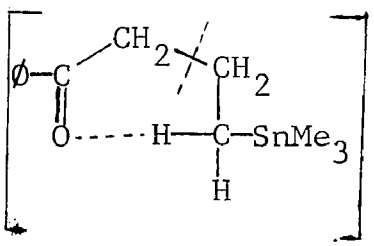
The ketone was photolysed according to procedures (b)

and (c). Table XIII gives the date and yields of the products. All of the runs were done in quartz apparatus and the solutions were degassed except where stated otherwise. The cyclohexane and benzene were dried with sodium. The iodine and sulfur additions were done as described for compound XI. The dimethyltin oxide and methane were determined in a method already discussed. When the toluene-sulfur solution was added in run No. 10, there was already considerable precipitate present giving a yield of dimethyltin oxide. Hydrogen peroxide was added in run No. 9 to insure complete formation of the oxide.

In reviewing the results of the photolysis in the table, it becomes evident that this reaction is similar to the other methyl ketone, XII. In the above case the main reaction appears to be the cleavage of the tin-carbon bond.

N. Mechanisms for the tin compounds

In comparing the photolysis of the tin compounds with the silicon compounds, there are striking differences. The type of products which are common to the photolysis of the ketones containing silicon are present only in small quantities in two of the ketones containing tin; i.e., to those with three methylene carbons between the carbonyl and tin atom (XI and XII). The formation of vinyltrimethyltin in both cases suggests that the Norrish Type II mechanism might occur to a small extent.



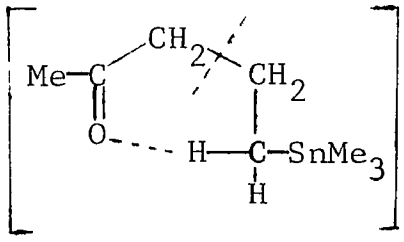


TABLE XIII

No.	Solvent	Time (hrs.)	Percent reacted	Conditions	$(Me_2SnO)_x$	CH_4
1	20% n-hexane	26	66	(b) in pyrex tube	-[a]	-[a]
2	71% ethanol	26	95	(b) in pyrex tube	-[a]	-[a]
3	69% benzene	26	91	(b) in pyrex tube	-[a]	-[a]
4	86% cyclohexane	34	58	(c)	43	28
5	80% cyclohexane	36	59	(c)	64	54
6	76% cyclohexane	35	58	(c) not degassed flushed with oxygen	6	15
7	76% cyclohexane	35	65	(c) not degassed flushed with argon	12	27
8	80% cyclohexane	22	53	(c)	none[c]	55
9	67% cyclohexane	27.5	90[b]	(c)	38[d]	63
10	69% cyclohexane	27.5	96[b]	(c)	24[e]	69

[a]These products were detected, but no yields were determined.

[b]A new lamp was used.

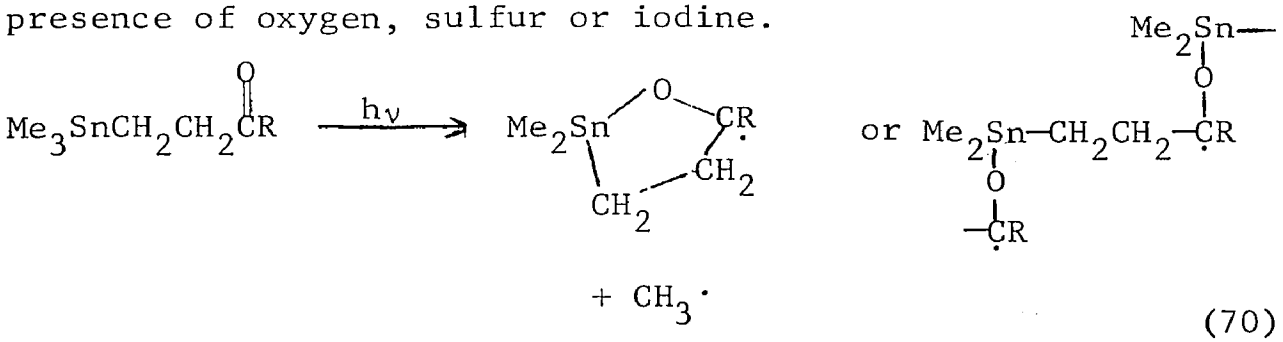
[c]Iodine was added to the photolysis products.

[d]The oxide was precipitated with hydrogen peroxide.

[e]Sulfur was added to photolysed products.

In all four tin compounds the major products were methane and apparently dimethyltin. This suggests a common mechanism in all cases. A question might arise as to how tin compounds which do not contain a chromophor, such as the ketone group, might react under the photolytic conditions of this work. To answer this question, the two intermediate nitriles, trimethyl-2-cyanoethyltin and trimethyl-3-cyanopropyltin, were photolysed as 50% solutions in cyclohexane for 56 hrs. There was no significant yield of dimethyltin oxide. Only a small precipitate resulted. Also, there was no methane evolved. The interesting observation in this case was that on the walls of the tube containing the former nitrile was formed a good tin mirror.

One conceivable mechanism which might be considered is attack of activated oxygen on the tin atom, which then eliminates a methyl radical. A second is internal conversion followed by transfer of the energy through the chain to the tin-carbon bond, which is then broken. Considering the former mechanism in more detail, the first step after excitation of the carbonyl group, would be the attack on the tin atom. The methyl radical would then be ejected. This radical could then extract a hydrogen atom from another molecule forming methane and a new radical which would be unstable decomposing in the presence of oxygen, sulfur or iodine.



(70)

If this mechanism could occur intermolecularly, then non-functional organotin compounds should react upon irradiation with common ketones. An experiment was run in order to test this possibility. Tetramethyltin was photolysed for 50 hrs. with equivalent amounts of ethyl methyl ketone (dried over anhydrous potassium carbonateand distilled), benzaldehyde, acetophenone and benzophenone in separate tubes with cyclohexane. Only in the tube containing benzaldehyde was any gas evolved. There was no formation of dimethyltin oxide upon exposure to air. The major change in any of the tubes was the formation of the pinacol in the tube containing the benzophenone.

One further experiment was done for detection of possible intermolecular reactions. In this case the tubes were degassed. One contained trimethyl-3-cyanopropyltin, ethyl methyl ketone and cyclohexane in 1:1:2 weight ratio. The other tube was identical except it did not contain a tin compound. Photolysis produced gas in both tubes. This shows that the ketone of itself produced gas. However, no dimethyltin oxide was formed in the tube containing the organotin compound upon exposure to the atmosphere. These experiments would indicate that the reaction is not intermolecular in character.

One difficulty with the first mechanism is that if the assumption were true as shown in Eq. (68), then there are three carbon-tin bonds yet intact. It is difficult to concieve how oxygen from the atmosphere could cause the cleavage of one of these bonds to form dimethyltin oxide so easily. The exact processes of this reaction are in general unclear and difficult to explain.

The second mechanism considered was the transfer of energy along the chain to break the tin-carbon bond leading to

the chain. It is conceivable that the trimethyltin radical could then eject a methyl radical forming dimethyltin in the presence of ultraviolet light. The methyl radical could then abstract a hydrogen from another molecule or fragment forming methane.

$$Me_3Sn(CH_2)_2COR \xrightarrow{h\nu} Me_3Sn\cdot + \cdot(CH_2)_2COR$$

$$Me_3Sn\cdot \xrightarrow{h\nu} Me_2Sn + Me\cdot \qquad (71)$$

$$Me\cdot + \cdot(CH_2)_2COR \text{ (or solvent)} \longrightarrow CH_4 + CH_2{=}CHCOR \xrightarrow{h\nu} \text{polymer} \qquad (72)$$

If vinyl and allyl ketones were formed, they would polymerize very rapidly catalyzed by the ultraviolet light. A tube of 30% vinyl methyl ketone in cyclohexane was photolysed and gave a 100% yield of polymer. Moureu and co-workers[26] reported that acrolein will completely solidify when exposed to ultraviolet light in 1.9 hrs. If this should be the mechanism then the detection of dimethyltin would be in its favor.

If the trimethyltin radical is present as proposed in the last mechanism, then it is conceivable that hexamethylditin might form. However, it was not detected in the products When a solution of hexamethylditin (30% wt.) was photolysed with acetophenone (15% wt.) in cyclohexane, the ditin rapidly reacted giving methane, and dimethyltin when the product mixture was exposed to the atmosphere. Both components completely reacted in 15 hrs., giving yields of 30% and 23% of the oxide

and methane, respectively. When hexamethylditin was photolysed in cyclohexane without any ketone, the yields of the oxide and methane were 23% and 12%, respectively. The hexamethylditin reacted to the extent of 88%. These experiments show that hexamethylditin would not be expected to be a major product even if the trimethyltin radical did form as an intermediate.

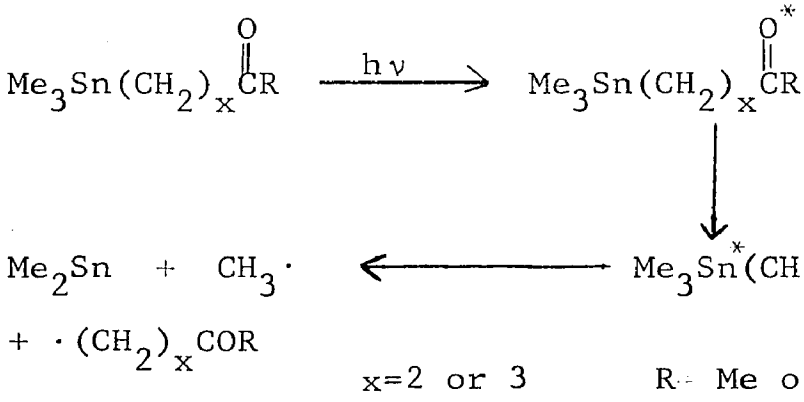
Another experiment which was performed to test for the presence of trimethyltin radicals was the photolysis of 4-(1-phenyl-1-oxobutyl)trimethyltin in the presence of bromo- and chlorocyclohexane. If the trimethyltin radical is present, it should give trimethyltin bromide or chloride. Kuivila and coworkers[27] have shown that trialkyltin radicals attack organic halides. The alkyl bromides are generally much more reactive than the alkyl chlorides. One must be cautious because trialkyltin halides react photochemically as reported in the Introduction.[15] Also, there is the question as to whether the ultraviolet light would decompose the radical to dimethyltin and methyl radical before the reaction occurred with the halide.

In this experiment two tubes were prepared. Each contained about 20% of ketone XI with about 35% of the halide (bromocyclohexane in one tube and chlorocyclohexane in the other) by weight. Cyclohexane made up the remainder of the weight. The tubes were photolysed 8 hrs. according to procedure (b). In the tube containing the chloride the methane and oxide were obtained in 34% and 11% yields, respectively. The chlorocyclohexane was completely unreacted. Not even a trace of trimethyltin chloride was detected. In the tube containing bromocyclohexane a 32% yield of methane was obtained and dimethyltin oxide was recovered after air-oxidation in a 5% yield. Though the chloride is not reactive enough to enter into the reaction under these conditions, the bromide definitely reacts. Trimethyltin bromide was obtained in a 17%

yield based on the ketone which reacted. The bromocyclohexane had reacted to the extent of 0.82 mole per 1.0 mole of reacted ketone. This would indicate that trimethyltin radicals were formed. But, it should be remembered that alkyl bromides themselves photolyse, forming bromine radicals which could then cleave the tin molecule.

An experiment was run to determine how bromocyclohexane would react with alkyltin compounds in the presence of ultraviolet light. Tetramethyltin (18%) was photolysed with bromocyclohexane (29%) in methylcyclohexane (53%). The tetramethyltin reacted only to the extent of 17%. For every mole of tetramethyltin which reacted, four moles of the bromide reacted and one mole of methane was formed. There was not even a trace of trimethyltin bromide detected by gas-liquid chromatography using the silicone oil 200 column. The tin was recovered as dimethyltin dibromide. This could indicate that the formation of trimethyltin bromide as described in the previous paragraph really comes from the trimethyltin radical proposed.

One further mechanism which can be considered is intramolecular sensitization. It is conceivable that the energy absorbed by the carbonyl could be transferred to the tin atom placing it into an excited electronic state, which then would react by cleavage of carbon-tin bonds.



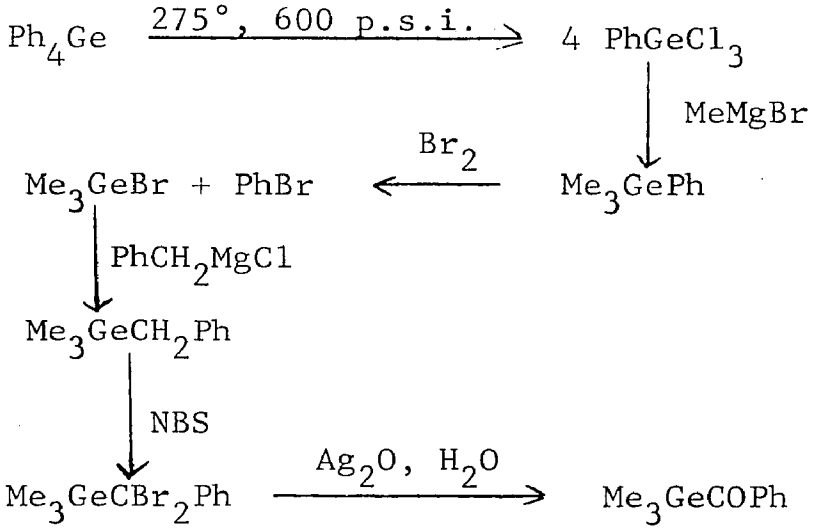
(73)

No attempt was made to distinguish this mechanism from the others mentioned.

O. Benzoyltrimethylgermane (XV)

There were three major pieces of synthetic work which did not succeed well inproducing compounds for photolysis. These will be discussed briefly for the sake of information.

One of these was an attempt to make an organogermanium compound for comparison with the tin and silicon compounds. The synthetic steps are reviewed in the following equations:

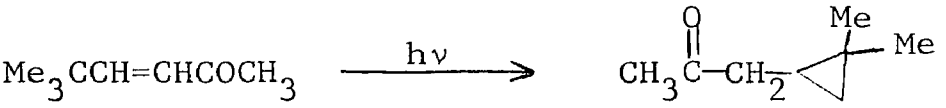


(74)

The yields were very poor in the last two steps which paralleled the procedure of Brook[22] on the preparation of similar silicon compounds. A considerable amount of benzyl bromide and trimethylgermanium bromide was recovered in the bromination step. The hydrolysis with water and silver acetate gave only 2-3% of a bright yellow liquid whose infrared spectrum was very similar to that of benzoyltrimethylsilane. Benzoyltrimethylgermane appeared to be less stable, and solutions of it decomposed in the presence of moisture rather rapidly. A sample was photolysed, but because of the impurities, the results were inconclusive; benzaldehyde was formed.

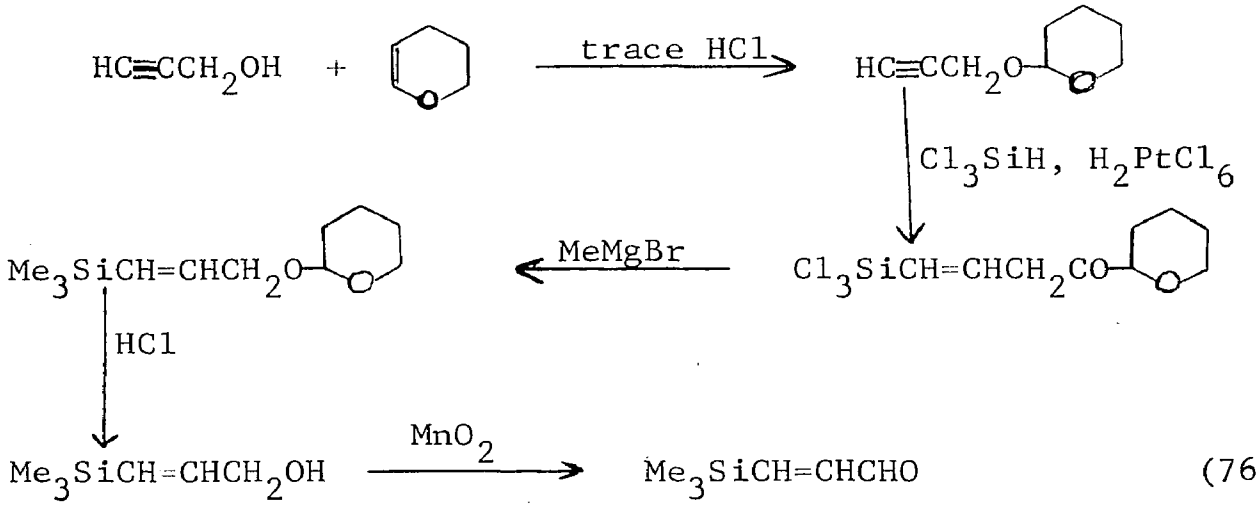
P. 3-(Trimethylsilyl)acrolein (XVI)

Yang and Yang[28] discovered a novel reaction upon the photolysis of 5,5-dimethyl-3-hexan-2-one.



(75)

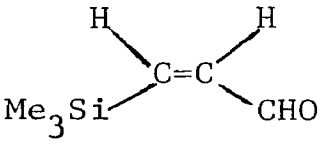
It should also be of interest to determine the effect that silicon might have on the photochemistry of such a compound. An attempt was made to prepare 3-(trimethylsilyl)acrolein by the following synthetic steps:

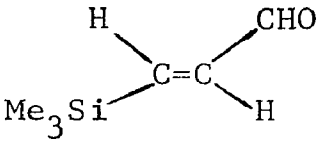


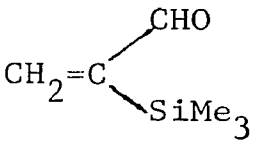
(76)

The second step went in such poor yield that little remained for the following steps. There was considerable evolution of hydrogen chloride in the second step indicating cleavage of the acetal. The final product had infrared spectrum with bands at 3040 (w), 2950 (s), 2825 (m), 1710 (w), 1680 (s), 1430 (m), 1360 (m), 1250 (broad, must be an overlap of the carbonyl and trimethylsilyl bands), 1090 (m), 1050 (m), 995 (m), 860 (s), 840 (s), 760 (m), and 695 (m) cm^{-1}. Investigation by gas-liquid chromatography using the silicone oil 200 column gave on large peak with two shoulders in an

approximate area ratio of 5:3:2. These may represent the three possible isomers.







It is, however, unlikely that the latter one would survive the hydrochloric acid solution used in hydrolyzing the acetal as it is a beta silyl aldehyde.

EXPERIMENTAL

Infrared Absorption Spectra - The infrared absorption spectra were determined using a Perkin-Elmer Model 21 infrared spectrophotometer with sodium chloride optics at the following settings: resolution, 927; response, 1; gain, 5-5; speed, 2.5-6; suppression, 0; scale, standard. The spectra of solids were determined as mulls in series 11-14, using Halocarbon oil from 1300-4000 cm^{-1} and Nujol from 650-1300 cm^{-1}.

Ultraviolet Absorption Spectra - The ultraviolet absorption spectra were obtained using a Perkin-Elmer Model 4000 recording spectrophotometer. Unless otherwise stated, the solvent was Fisher reagent-grade methanol.

Analytical Data - Microanalyses were determined by Galbraith Microanalytical Laboratory, Knoxville, Tennessee.

Nuclear Magnetic Resonance Spectra - The nuclear magnetic resonance spectra were determined using a Varian A-60 instrument. Unless otherwise stated, the chemical shifts are in ppm from tetramethylsilane used as an internal standard.

Melting Points - The melting points were taken either in capillary tubes in oil bath or by Fisher-Johns Melting Point Apparatus. They are uncorrected.

Vapor Phase Chromatography - All of the analytical work and some of the separation and purification were carried out on a F & M Model 300. The columns most commonly used were 20% Apiezon L on chromasorb and 5% silicone oil 200 on haloport F. Some of the separation work was carried out on an Aerograph Autoprep Model 700.

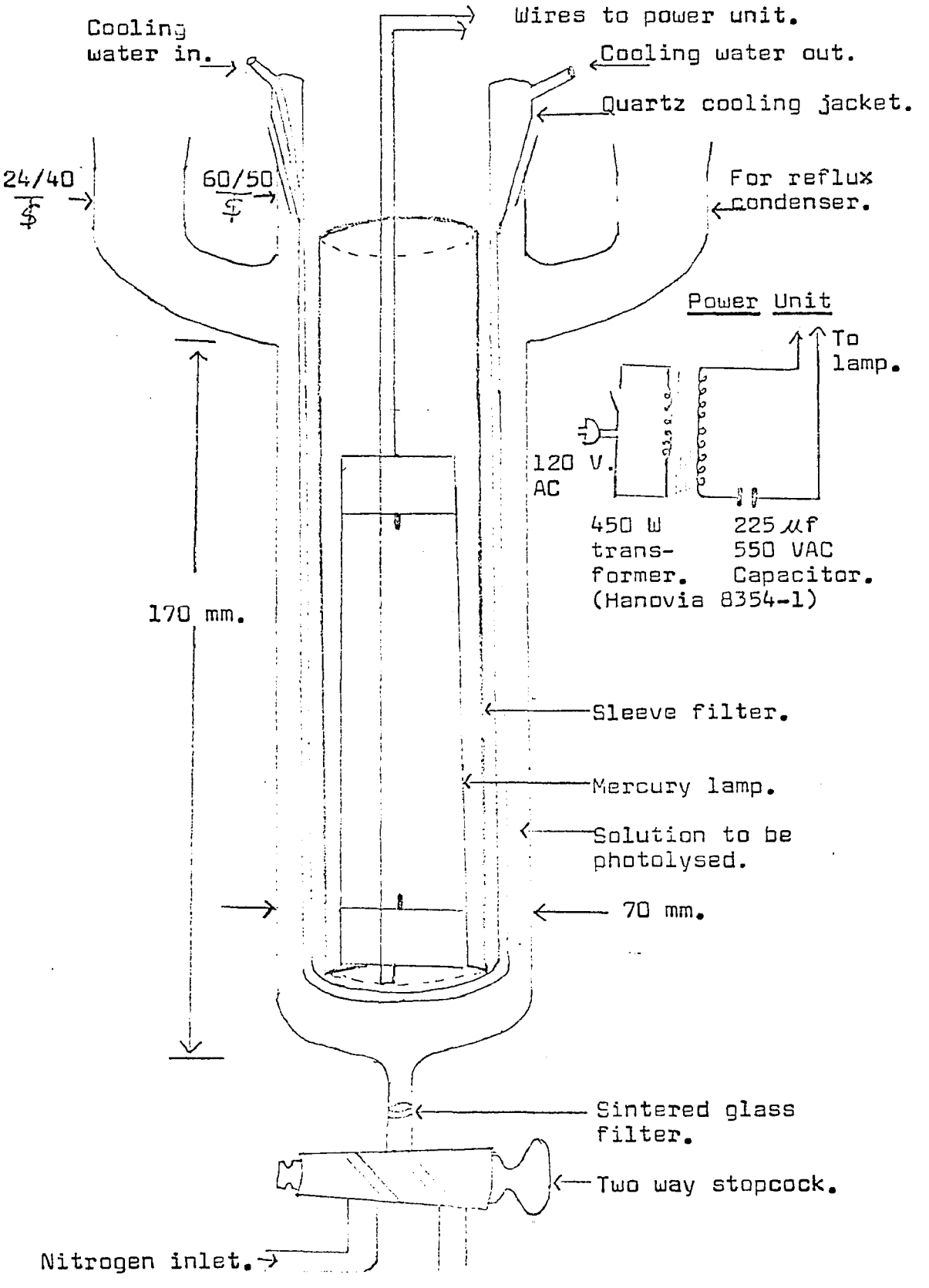
Photolysis Procedures - The photolysis experiments were carried out in three different ways.

(a) Large scale photolysis. Figure I shows the apparatus used. In this setup the solution to be photolysed was placed in the outer vessel. Nitrogen was bubbled through to provide stirring. The outer vessel which was used in most experiments contained 170 ml. of liquid. A trap cooled by carbon dioxide-acetone or liquid nitrogen was generally employed to collect the more volatile products.

(b) Photolysis in quartz tubes. Figure II shows the apparatus used. The solutions to be photolysed were placed in tubes 15 cm. long and 2 to 8 mm. inside diameter which were placed in the setup as shown. Water was used in the apparatus as a medium for transporting the heat to the cooling jacket. The temperature of the cooling water varied with the season, ranging from 31° to 38°. For preliminary runs the tubes were stoppered with rubber policemen. In most cases this was satisfactory. However, in those cases in which oxygen and moisture affected the products, the rubber policemen were not suitable. Rubber balloons were attached to the mouth of the tubes in the case of the tin compounds for collecting evolved gases. In all cases the tubes were flushed with Matheson argon (99.998% pure) before irradiation.

(c) Degassed photochemical experiments. Figure III shows the apparatus used. In these cases, the solution to be photolysed was placed in the pear-shaped bulb. The liquid was frozen by cooling with either carbon dioxide-acetone or liquid nitrogen depending on the temperature needed to freeze the mixture. The tube was evacuated to 1 mm. Then the stopcock was closed and the solid was allowed to warm up and melt releasing the dissolved gases. This was repeated four times.

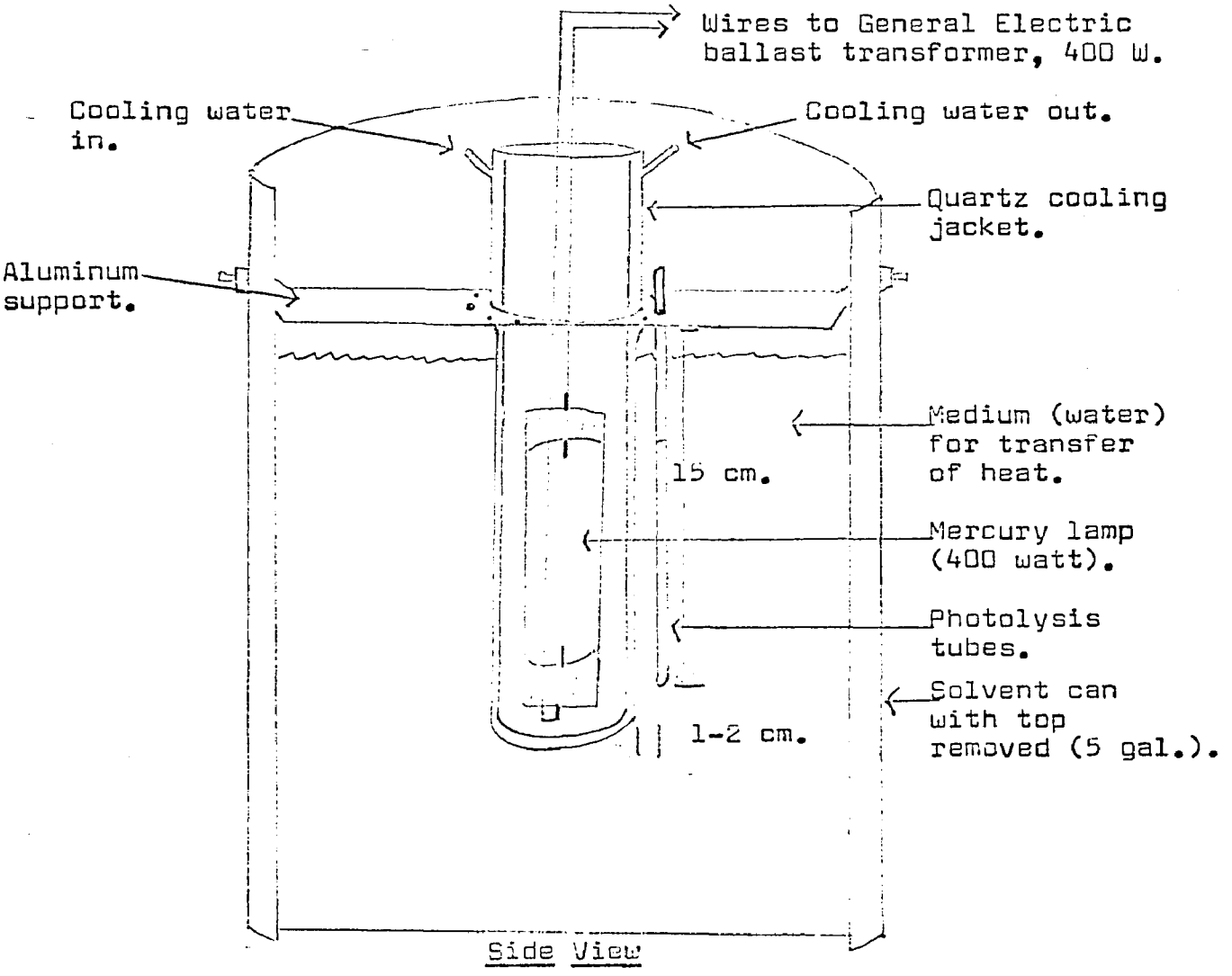
FIGURE I



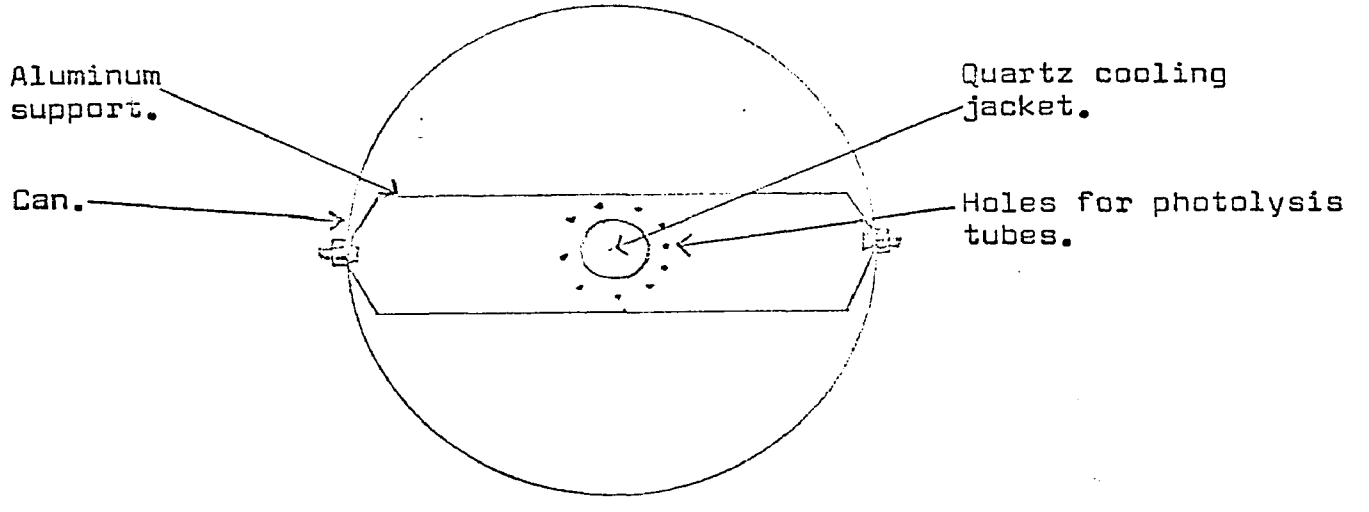
Apparatus for Procedure (a)

Figure II

Apparatus for Procedure (b)



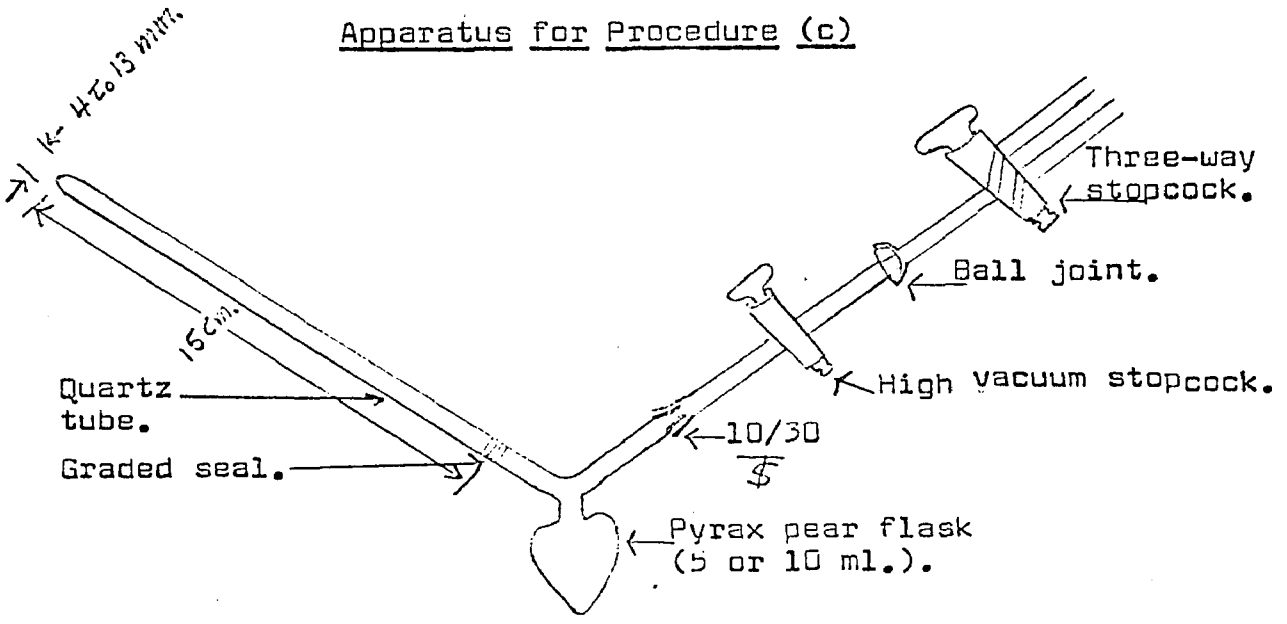
Side View



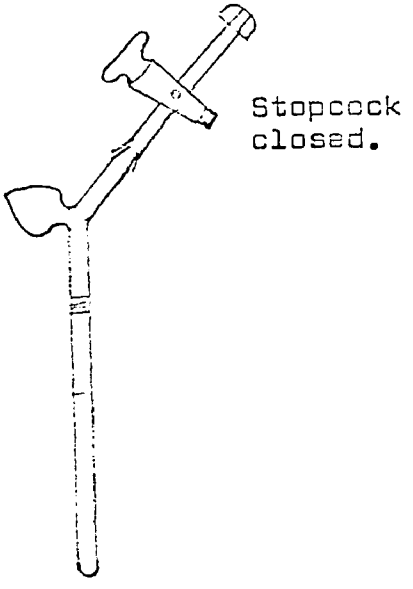
Top View

Figure III

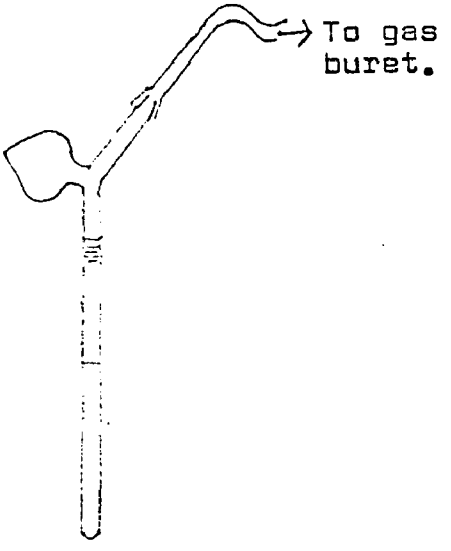
Apparatus for Procedure (c)



In decassing position



Photolysis set-up if no gas is produced.



Photolysis set-up if gas is produced.

The liquid was then allowed to drain into the quartz tube and photolysed as described in part (b). In the cases where there was no evolution of gas, the degassing tube with vacuum stopcock closed was inserted into the photolysis system as a unit. If gases were volved, a gas buret which had been flushed with argon was attached for measuring the volume of the gas evolved. To minimize the presence of mercury vapor which might effect the photolysis, a 2 cm. layer of the high boiling bis(2-ethoxyethyl)ether was placed on top of the mercury in the gas buret.

Ultraviolet Lamps - All of the large volume photochemical work was done using a Hanovia 450 watt lamp no. 679A. The spectral characteristics are given in Table XIV.

TABLE XIV

Characteristics of Hanovia Lamp 679A

Region	Wave length	Radiated energy (watts)
Far U.V.	220-280	27.0
Middle U.V.	280-320	28.7
Near U.V.	320-400	28.0
Visible	400-600	75.7
Infrared	1000-1400	16.4
	Total radiated energy	175.8

Watts - 450
Volts - 125 to 140
Amps - 3.7

Vycor 7910 and pyrex 7740 sleeve filters were used as described in some of the photochemical reactions. Figure IV, which was taken from the Hanovia brochure, indicates the transmission of irradiation at different wave lengths for the different filters.

In the work which was done with the small tubes [procedures (b) and (c)], a General Electric 400 watt lamp no. H400 A-33-1 was used. The outer glass was broken from these street lamps and the metal structures and wires were removed or manipulated so as to allow the lamp to fit into the cooling jacket. With this lamp there was no room remaining in the cooling jacket for filters. Filtering was achieved by the use of quartz, vycor or pyrex reaction tubes.

Isolation of Photolysis Products for Identification - All products which could be collected by gas-liquid chromatography were obtained in this manner for proof of structure by infrared spectrum, molecular weight, etc. The three products, vinyltrimethylsilane, hexamethyldisiloxane and biacetyl, which are very volatile, were obtained by distillation. The solid products were separated by column chromatography as described in each particular case. The gas was collected in balloons for infrared spectra. After the products were identified, yields were determined by gas-liquid chromatography whenever possible.

2-Sila-2,2-dimethylhexan-5-one (VII) - To a Grignard reagent prepared from 35 g. (1.46 moles) of magnesium and methyl bromide (Matheson) in 300 ml. of ether was added dropwise a solution of 54.0 g. (0.29 mole) of β-trichlorosilylpropionitrile (gift from Dow Corning or Union Carbide) in 150 ml. of ether. The mixture was refluxed with occasional stirring for 15 hrs. Hydrolysis was achieved by slowly adding

Figure IV

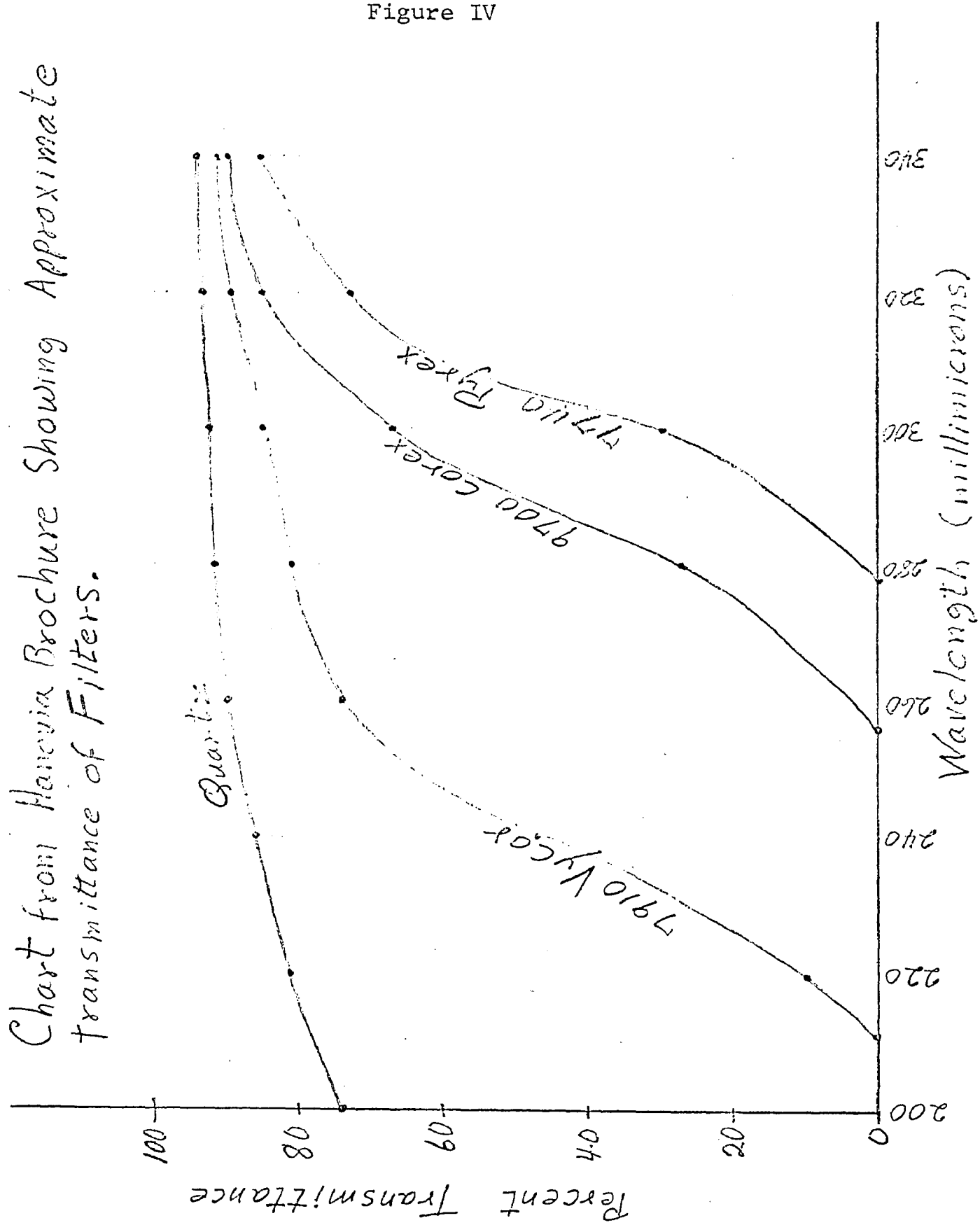


Chart from Hanovia Brochure Showing Approximate transmittance of Filters.
Quartz
7910 Vycor
9700 Corex
7740 UV Pyrex
Percent Transmittance
100
80
60
40
20
0
200
220
240
260
280
300
320
340
Wavelength (millimicrons)

100 ml. of saturated ammonium chloride solution. The mixture was then acidified with 18% hydrochloric acid until the precipitate had dissolved. The ether layer was washed with water and dried over anhydrous magnesium sulfate. After removal of the ether, the ketone was distilled through a 300 mm. column packed with glass helices; b.p. 73-75°/15 mm. The ketone was obtained in a 32% yield (13 g.).

5-Sila-5,5-dichlorohexanonitrile - To a refluxing mixture of 31.3 g. (0.45 mole) of allyl cyanide (Aldrich) and 0.50 g. of 5% platinum on charcoal (Engelhard) was added dropwise over a period of 2 hrs. 57.0 g. (0.5 mole) of methyldichlorosilane (Union Carbide). The mixture was refluxed 17 hrs. Distillation through a 15 cm. Vigreux column gave 56 ml. of the nitrile; b.p. 132-133°/20 mm. The moisture sensitive compound was used without further purification.

2-Sila-2,2-dimethylheptan-6-one (V) - To a stirred Grignard reagent prepared from 27.0 g. (1.08 mole) of magnesium and methyl bromide in 300 ml. of dry ether was added dropwise 56 ml. (0.4 mole) of the 5-sila-5,5-dichlorohexanonitrile in 75 ml. of dry ether. The mixture was refluxed 9 hrs. and then hydrolyzed with 50 ml. of saturated ammonium chloride solution. The ether solution was washed with water, dried over anhydrous magnesium sulfate and distilled, yielding 27 g. (38% based on the allyl cyanide) of the ketone; b.p. 85-86°/15 mm.

Vinyltrimethylsilane - To a stirred Grignard reagent prepared from 28.0 g. (1.17 moles) of magnesium and methyl bromide in 250 ml. of dry ether was added dropwise over a period of 2 hrs. 58.0 g. (0.35 mole) of vinyltrichlorosilane (gift from Union Carbide). The excess Grignard reagent was destroyed with 50 ml. of saturated ammonium chloride solution.

The ether layer was washed with water and dried over anhydrous magnesium sulfate. Distillation slowly through a 25 cm. column packed with glass helices gave 21 g. (60%) of the silane containing 10-15% ether; b.p. 52°.

2-Sila-2,2-dimethyl-5-phenylpentan-5-one (VI)[13]- (a) A mixture of 21.0 g. (0.21 mole) vinyltrimethylsilane and 3.62 g. benzoyl peroxide with 20 ml. toluene to help dissolve the peroxide was added dropwise to 63.0 g. (0.59 mole) freshly distilled benzaldehyde (Fisher). The mixture was refluxed 15 hrs. Flash distillation gave 9 ml. over a boiling range of 120-140°/20 mm. The benzaldehyde impurity was air oxidized over a period of 2 months. Further distillation through a 15 cm. Vigreux column gave 5.3 g. (12%); b.p. 130° per 15 mm.

(b)[15] To a Grignard reagent made from 13.0 g. (0.54 mole) of magnesium, 85.0 g. (0.54 mole) of bromobenzene (Fisher), and 150 ml. of dry ether was added 52.3 g. (0.40 mole) 2-sila-2,2-dimethylpentan-5-nitrile within one-half hr. with stirring. The mixture was refluxed for 1 hr. The complex was hydrolyzed by pouring into 80 ml. of a saturated solution of ammonium chloride with sufficient ice to moderate the reaction, and then acidified with 18% hydrochloric acid. The ethereal layer was washed with water and saturated sodium bicarbonate solution before drying over anhydrous magnesium sulfate. Distillation gave 56 g. (68%) of the ketone; b.p. 134-135°/15 mm. The infrared spectra of the ketones obtained in (a) and (b) were identical.

2-Sila-2,2-dimethylpentyl-5-nitrile - A mixture of 112 g. (0.59 mole) β-trichlorosilylpropionitrile in 100 ml. ether was added dropwise within 45 min. to a stirred Grignard reagent prepared from 44.0 g. (1.83 moles) of magnesium and methyl bromide in 300 ml. of dry ether. The mixture was immediately pured into 20 ml. of saturated ammonium chloride

solution with sufficient ice to cool the reaction. The ethereal layer was washed with water and dried over anhydrous magnesium sulfate. After removal of the ether under vacuum, distillation gave 57 g. (74%) of the nitrile; b.p. 60-69°/25 mm.

2-Sila-2,2-dimethyl-6-phenylhexan-6-one (IV) - To a boiling mixture of 62.6 g. (0.90 mole) allyl cyanide (Aldrich) and 0.60 g. of 5% platinum on carbon was added dropwise in three hours 106 g. (0.92 mole) of methyldichlorosilane. This was then refluxed for 10 hrs. Distillation gave 152 g. (92%) of 5-sila-5,5-dichlorohexanonitrile; b.p. 145°/11 mm.

To 5-sila-5,5-dichlorohexanonitrile (0.83 mole) in 300 ml. of ether was added dropwise a Grignard reagent prepared from 47 g. (1.9 moles) of magnesium and methyl bromide in 500 ml. of dry ether. The mixture was immediately poured on 10 g. of ammonium chloride with sufficient ice to cool the reaction. The ethereal layer was washed with water and dried over anhydrous magnesium sulfate. After removal of the ether, distillation of 5-sila-5,5-dimethylhexanonitrile gave 87 g. (75%); b.p. 90-95°/11 mm.

The 5-sila-5,5-dimethylhexanonitrile was added dropwise to phenylmagnesium bromide prepared from 20 g. (0.82 mole) of magnesium and 126 g. (0.80 mole) of bromobenzene (Fisher reagent). After refluxing for 2 hrs., the mixture was poured into 15 g. of ammonium chloride with sufficient ice to cool the reaction. The ethereal layer was washed successively with 10% sodium carbonate and saturated sodium chloride solution. Distillation gave 103 g. (52%) of the crude ketone. The ketone was redistilled for further purification; the faction boiling at 155°/21 mm. was collected. The infrared spectrum of this

compound (pure liquid) had bands at 3030 (w), 2930 (s), 2880 (m), 1680 (s), 1598 (m), 1580 (w), 1247 (s), 1220 (m), 970 (m), 855 (s), 735 (m), 690 (m) cm^{-1}. The ultraviolet spectrum (n-hexane) had a $\lambda_{max.}$ at 237.5μm ($\mathcal{E}$ = 15,000). The NMR spectrum of this compound had peaks at 8.00 (multiplicity of 4, area 2), 7.42(4,3); 2.87(3,2); 1.70(8,2); 0.54(6,2); 0.00(1.9) ppm from the Me_3Si- group proton peak.

Anal. Calcd.: C, 70.80; H, 9.15; Si, 12.75. Found: C, 70.86; H, 9.20; Si, 12.90.

2,3-Diphenylbutane-2,3-diol[29] - A mixture of 11.2 g. (0.093 mole) of acetophenone dried over calcium chloride for one day, 6.0 g. (0.22 g. atom) of aluminum foil, 0.4 g. of mercuric chloride, 75 ml. of absolute ethanol and 75 ml. of dry benzene were refluxed for 5 hrs. The mixture was hydrolysed by pouring on sufficient ice to cool the reaction. The mass was washed with benzene and filtered. The crystals were recrystallized from a benzenecyclohexane (1:1) mixture. Only a small amount, m.p. 125-127°, was obtained after several recrystallizations.

Chloromethyltrimethylsilane - A solution of 160 g. (1.12 moles) of chloromethyldimethylchlorosilane in 200 ml. of dry ether was added over a period of 30 min. to a Grignard reagent prepared from 30.0 g. (1.23 moles) of magnesium and methyl bromide in 300 ml. of dry ether. The mixture was poured on 10 g. of ammonium chloride with sufficient ice to cool the reaction. The ethereal layer was washed with water, dried over 5 g. of anhydrous magnesium sulfate and distilled through a column packed with glass helicies (25x250 mm.) yielding 125 g. (91%) of the product; b.p. 96-98°.

Addition of methyldichlorosilane to methylvinyl ketone - A mixture of 27.9 g. (0.25 mole) of methyldichlorosilane (Union Carbide), 14.0 g. (0.20 mole) of methylvinyl ketone (Matheson, Coleman and Bell), and 0.10 g. of 5% platinum on charcoal was refluxed 47 hrs. The pot temperature rose from 57° to a constant 74°. The starting materials were removed at reduced pressure leaving 75% of the total weight used. Attempted distillation of this residue gave only a small amount of a volatile material which was not characterized.

Iodotrimethylsilane - A mixture of 30.5 g. (0.19 mole) of hexamethyldisiloxane, 5.1 g. (0.20 g. atm.) of aluminum filings, and 67.1 g (0.26 mole) of iodine was warmed on the steam bath until the reaction had started. The mixture was then refluxed for 1.5 hrs. and distilled yielding 51 g. 67%) of the silane; b.p. 101-106°/760 mm.

2-Sila-2,2-dimethyl-5-cyclohexyl-5-phenylpentan-5-ol - To a Grignard reagent prepared from 0.75 g. (0.031 mole) of magnesium and 5.1 g. (0.031 mole) of bromocyclohexane (Matheson, Coleman & Bell) in 50 ml. of dry ether was added 3.5 g. (0.02 mole) of 2-sila-2,2-dimethyl-5-phenylpentan-5-one. After stirring for 30 min. the mixture was poured on 1 g. of ammonium chloride with sufficient ice to cool the reaction. The ether layer was washed with water and dried over anhydrous magnesium sulfate. After removal of the ether, the mixture was eluted with pentane through a dry packed column of silicic acid and infusorial earth (2:1). The yield was estimated to be 35% by spot size on thin layer chromatography. The thick oil never did crystalize. The infrared spectrum of this compound (pure liquid) had bands at 3570 (s), 3100 (w), 2980 (s), 1505 (m), 1454 (m), 1245 (s),

1180 (m), 860 (s), 835 (s), 785 (m), and 695 (m) cm^{-1}. The NMR spectrum had peaks at 7.34 (multiplicity-2, area integration-5), 2.55(1,1); 1.64(5,6); 1.10(m,1); 0.40(8,2); 0.00(1,9) ppm from the Me_3Si- group proton peak.

Anal. Calcd.: C, 74.40; H, 10.42; Si, 9.68. Found: C, 74.64; H, 10.68; Si, 9.41.

Trimethylsilylacetone (IX)[21] - A Grignard reagent prepared from 36.0 g. (0.29 mole) of chloromethyltrimethylsilane and 7.2 g. (0.29 mole) of magnesium in 100 ml. dry ether was added with stirring over a period of 2 hrs. to 22.8 g. (0.22 mole) of acetic anhydride (freshly distilled) in 100 ml. of dry ether. The reaction vessel was submerged in a carbon dioxide-acetone bath. The mixture was stirred for 4 hrs. and then allowed to warm up to room temperature whereupon 100 ml. of 10% ammonium chloride was added dropwise. The ether layer was removed, washed with saturated sodium bicarbonate solution and dried over anhydrous magnesium sulfate. Distillation gave 13 g. (47%) of product; b.p. 54-61°/52 mm.

Pentylsilane[30]- To 5.2 g. (0.13 mole) of lithium aluminum hydride in 50 ml. of di-n-butyl ether (Eastman) was added dropwise in 25 min. with stirring 26.7 g. (0.13 mole) of pentyltrichlorosilane (Union Carbide) in 25 ml. of di-n-butyl ether. The next day the silane was distilled through a column packed with glass helices (24x200 mm.); 9.9g.(75%); b.p. 76-78°/760 mm.

Cyclohexylcarbinol[31]- To a Grignard reagent made from 48.9 g. (0.30 mole) of bromocyclohexane (Eastman) and 7.9 g. (0.30 mole) of magnesium in 100 ml. of anhydrous ether was added 9.0 g. (0.30 mole) of paraformaldehyde which had been dried over phosphorus pentoxide. The mixture was stirred with refluxing for 5 hrs. The complex was added to ice, then

30 ml. of 98% sulfuric acid in 100 ml. water was added and the mixture was steam distilled. To the distillate was added 40 g. of sodium chloride and the non-aqueous layer was extracted with ether. Distillation gave 10.6 g. (31%) of the alcohol; b.p. 90-93°/20 mm.

Cyclohexylchloromethane - Into 40.0 g. (0.34 mole) of thionyl chloride (Fisher) was added dropwise over 10 min. period 10.6 g. (0.093 mole) of cyclohexylcarbinol. The mixture was refluxed one hr. The excess thionyl chloride was removed by vacuum. Distillation gave 7.25 g. (59%) of the chloride; b.p. 68-71°/26 mm.

2-Sila-2,2-dimethyl-4-cyclohexylbutane - A mixture of 7.25 g. (0.055 mole) of cyclohexylchloromethane and 15.15 g. (0.12 mole) of chloromethyltrimethylsilane were mixed and added to 4.14 g. (0.18 g. atm.) of thinly sliced sodium in 75 ml. of anhydrous ether. After 14 hrs., methanol was added to decompose the excess sodium. The mixture was distilled giving 3.5 g. boiling at 84-117°/21 mm. The compound was purified by gas-liquid chromatography. The chromatogram indicated that the mixture contained 60% of the product, corresponding to a yield of 21% (2.1 g.). The infrared spectrum of the compound (pure liquid) had bands at 2920 (s), 2860 (m), 1450 (s), 1246 (s), 860 (s), 833 (s), 745 (m), and 685 (m) cm^{-1}. The NMR spectrum had peaks at 1.75 (m), 1.14 (m), 0.68 (8), and 0.00 (1) ppm downfield from the peak for the Me_3Si- protons.

Anal. Calcd.: C, 71.62; H, 13.14; Si, 15.24.
Found: C, 71.63; H, 13.39; Si, 15.47.

Benzoic anhydride[32] - A mixture of 76 g. (0.62 mole) of benzoic acid, 70 ml. (of the total 1.12 moles or 105 ml. used) of acetic anhydride and 5 drops of 85% phosphoric acid was heated slowly until acetic acid distilled from a 60 cm. column. The remaining acetic anhydride was added when an equal volume of acid had been collected. When the collection temperature had reached 140°, the pressure was reduced and the crude anhydride was collected at 223°/21 mm. Crystallization from pentane gave 32 g. (46%) of the product, m.p. 38-40°.

Trimethylsilylacetophenone (VIII) - A Grignard reagent made from 12. 27 g. (0.10 mole) of chloromethyltrimethylsilane and 21.43 g. (0.10 mole) of magnesium in 100 ml. of dry ether was added dropwise to a stirred mixture containing 20.4 g. (0.09 mole) of benzoic anhydride in 100 ml. of dry ether in a carbon dioxide-acetone bath over a period of 45 min. The mixture was stirred another 45 min. and allowed to warm up. When the temperature of the reaction mixture had reached -15°, 100 ml. of 10% ammonium chloride solution was added dropwise. After washing the ether layer with saturated sodium bicarbonate and sodium chloride solutions the ether was removed at reduced pressure. Distillation gave 12 g. (73% yield) of the ketone; b.p. 130-134°/20 mm. The infrared spectrum of the compound (pure liquid) had bands at 3070 (w), 2970 (s), 2910 (m), 1668 (s), 1600 (m), 1580 (w), 1450 (m), 1415 (m), 1248 (s), 1260 (s), 1105 (m), 1010 (w), 850 (s), 753 (m), 705 (m) cm^{-1}. The ultraviolet spectrum (in sodium dried n-hexane) had a $\lambda_{max.}$ of 235.5mμ (ϵ 15,000). The NMR spectrum had peaks at 8.05 (multiplicity of 4), 7.41 (4), 2.72 (1), 0.07 (1) ppm from tetramethylsilane.

Anal. Calcd.: C, 68.67; H, 8.39; Si, 14.62.
Found: C, 68.44; H, 8.14; Si, 14.89.

Addition of methyldichlorosilane to allyl chloride - To a mixture of 54.0 g. (0.69 mole) of 3-chloropentene (Eastman), 0.1 g. of 5% platinum on charcoal and 0.1 g. of 2,6-bis(t-butyl)cresol was refluxed 27 hrs. The product was distilled at 95-101°/42 mm. The silane was obtained in a 60% yield (78 g.).

1-(Trimethylsilyl)-3-chloropropane[16] - To a Grignard reagent prepared from 21 g. (0.89 mole) of magnesium and methyl bromide in 300 ml. of dry ether was added slowly 80 g. (0.41 mole) of 1-(methyldichlorosilyl)-3-chloropropane in 100 ml. of dry ether. The complex was poured on 10 g. of ammonium chloride with sufficient ice to cool the reaction. The ether layer was dried over 10 g. anhydrous sodium sulfate. The product was distilled through a column (13x270 mm.) packed with glass helices; b.p. 68-69°/43 mm. The silane was obtained in a 69% yield (42.5 g.).

1-(Trimethylsilyl)-3-iodopropane[16] - A mixture of 40 g. (0.27 g. atm.) of sodium iodide and 32.1 g. (0.206 mole) of 1-(trimethylsilyl)-3-chloropropane in 400 ml. acetone which had been dried according to Vogel (his book p. 171) was refluxed for 15 hrs. The acetone was distilled. The iodo compound was then obtained in an 87% yield (43.3 g.); b.p. 75-83°/40 mm.

2-Sila-2,2-dimethyl-7-phenylheptan-7-one[16] - A solution of sodium ethoxide was made from 3.75 g. (0.163 g. atom) of sodium in 1000 ml. of absolute ethanol. To this was added 31.3 g. (0.163 mole) of ethyl benzoylacetate (Matheson, Coleman & Bell). The solution was then added to 39.0 g. (0.161

mole) of 1-(trimethylsilyl)-3-iodopropane in 300 ml. of absolute ethanol during a period of 50 min. A solution of 37% hydrochloric acid was added until slightly acidic (10 ml. was required). The ethanol was distilled. The product was extracted with 100 ml. of ether. After removal of the ether at reduced pressure, decarboxylation was attempted by heating with concentrated hydrochloric acid without success. Decarboxylation was achieved by heating the ester with 10 m. of water, 10 ml. of 95% ethanol and 7 g. of potassium hydroxide for 3 hrs. Distillation gave 8 g. (40% yield based on iodo compound consumed; 18% was recovered) of the ketone; b.p. 148-152°/1 mm. The infrared spectrum of the compound (pure liquid) had bands at 3060 (w), 2940 (s), 1683 (s), 1592 (m), 1580 (m), 1449 (s), 1410 (m), 1245 (s), 1210 (s), 860 (s), 830 (s), 745 (m), 685 (m) cm^{-1}. The ultraviolet spectrum (in n-hexane) had a $\lambda_{max.}$ at 237.5mμ(ε = 15,000). The NMR spectrum had peaks at 7.99 (multiplicity of 5), 7.35 (4), 2.85 (3), 1.16 (10), 0.46 (3), 0.00 (1) ppm from the peak of the Me_3Si- protons.

Anal. Calcd.: C, 71.72; H, 9.47;, Si, 11.99.
Found: C, 71.63; H, 9.57; Si, 11.87.

Benzyltrimethylsilane - A mixture of 163 g. (1.5 mole) of chlorotrimethylsilane (Union Carbide), 152 g. (1.2 mole) of benzyl chloride (Baker & Adamson reqgent) was added to 40.0 g. (1.65 moles) of magnesium in 40 ml. of dry ether. The mixture was refluxed for 15 hrs. Distillation gave 150 g. (47%) of the silane; b.p. 95-105°/48 mm.

α,α-Dibromobenzyltrimethylsilane[22] - To a mixture of 100 g. (0.606 mole) of benzyltrimethylsilane, 23.1 g. (1.28 moles) of N-bromosuccinimide (Fisher, reagent), and 450 ml. of chloroform was added 0.1 g. of benzoyl peroxide. The initial exothermic reaction was controlled by cooling

with an ice bath. The mixture was refluxed for 42 hrs. During reflux, a total of 0.4 g. of the peroxide was added in four separate portions. Distillation, after removal of the succinimide by filtration, gave 163 g. (83%) of the silane; b.p. 105-125°/3 mm. Further purification was achieved by crystallization from ethyl acetate at 0°.

Benzoyltrimethylsilane[23] - To a mixture containing 89.0 g. (0.28 mole) of α,α-dibromobenzyltrimethylsilane, 150 ml of 95% ethanol, 75 ml. of acetone and 35 ml. of water was added with stirring 95.1 g. (0.57 g. atm.) of silver acetate (Mallinckrodt). The reaction was only slightly exothermic. After standing at room temperature for 12 hrs., the mixture was filtered and most of the solvent removed under reduced pressure The mixture was extracted with ether. The ether layer was removed and dried over anhydrous sodium sulfate. Distillation gave 53 g. (52%) of the bright yellow ketone, boiling at 94-97°/9 mm. As the ketone is unstable to moisture, the product was stored in sealed glass ampules.

Phenylsilane - To a solution containing 14.8 g. (0.39 mole) of lithium aluminum hydride in 275 ml. of dry ether was added dropwise over 1 hr., 100 g. (0.47 mole) phenyltrichlorosilane (Union Carbide) in 80 ml. of dry ether. After refluxing for one additional hour, the mixture was distilled through a column (24x250 mm.) packed with glass helices. The silane was obtained in a 75% yield (3 .3 g.); b.p. 46°/1 mm.

1-Sila-1-phenyl-4,4-dimethoxybutane[30] - A mixture of 35.0 g. (0.33 mole) of phenylsilane, 18.4 g. (0.18 mole) of 3,3-dimethoxypropene-1 (gift from Shell Development Co.), and 1.0 g. of t-butyl peroxybenzoate was heated on the steam bath for 48 hrs. Distillation gave 26.1 g. (69% yield based on the acetal); b.p. 95-105°/10 mm. Further purification was obtained

by eluting with pentane through a column packed dry with 2:1 silicic acid and infusorial earth. The infrared spectrum of this compound (pure liquid) contained bands at 3034 (w), 2920 (s), 2820 (s), 2135 (s), 1425 (m), 1360 (m), 1115 (m), 1055 (m), 925 (m), 850 (m), 694 (m) cm^{-1}. The NMR spectrum contained bands at (multiplicity, integrated area) 7.55 (4,2), 7.25 (4,3), 4.43 (3,2), 4.27 (3,1), 3.18 (1,6), 1.65 (10-12,2), 0.93 (10-12,2) ppm from tetramethylsilane.

Anal. Calcd: C, 62.79; H, 8.63; Si, 13.36.
Found: C, 63.01; H, 8.58; Si, 13.49.

4 -Sila-4-phenylbutanal - A mixture of 17 g. (0.081 mole) of 1-sila-1-phenyl-4,4-dimethoxybutane, 0.5 g. of oxalic acid dihydrate and 1.1 g. (0.061 mole) water in 110 ml. of acetone was refluxed 90 hrs. The infrared spectrum of the product mixture contained strong alcohol, carbonyl and silicon-hydrogen stretching bands. Attempted distillation, however, gave only foam rubber at 1 mm. and 120°. Elution with pentane through a column packed with glucose gave alcohol-free aldehyde with some of the acetal present. Elution through silica with pentane gave decomposition. The infrared spectrum of the material from the glucose column contained bands at 3050 (m), 2910 (s), 2705 (m), 2140 (s), 1715 (s), 1430 (m), 1115 (s), 933 (s), 860 (s), 840 (s), 730 (m) and 694 (s) cm^{-1}. The NMR spectrum (aldehyde band not taken) had bands at 7.42 (multiplicity of 4), 4.41 (3), 1.64 (12) and 0.96 (7-8) ppm from TMS.

1,2-Dibenzoylethane - A mixture of 24.0 g. (0.30 mole) of succinic acid, 63 g. (0.53 mole) of thionyl chloride and 1.5 g. of anhydrous zinc chloride was refluxed for 2.5 hrs. The excess thionyl chloride was removed with reduced pressure. The succinyl chloride was then treated with 70 g. (0.90 moles)

50 ml. water and the mass was extracted with ether. The material remaining after evaporation of the ether was eluted through a column packed with basic alumina. A small quantity was obtained for infrared spectrum and chromatographic work, m.p. 143-145°.

1,4-bis(Trimethylsilyl)butane[35] - To a Grignard reagent prepared from 7.5 (0.30 mole) of magnesium and 30.0 g. (0.14 mole) of 1,4-dibromobutane (Matheson, Coleman & Bell), and 100 ml. of tetrahydrofuran (distilled from lithium aluminum hydride) was rapidly added dropwise 49.0 g. (0.45 mole) of chlorotrimethylsilane (Union Carbide). To the mixture was added 40 ml. of water and 10 ml. of concentrated hydrochloric acid. Distillation gave two layers at 70-78°/11 mm. The upper layer was the desired silane, 12 g. (27%).

Ethoxytrimethylsilane - To a mixture containing 6.4 g. (0.14 mole) of absolute ethanol, 15.0 g. (0.14 mole) of trimethylchlorosilane (Union Carbide) and 30 ml. of bis-(2-ethoxyethyl)ether was added 3.3 g. (0.14 g. atm.) of sodium. The mixture was stirred cooling periodically with an ice bath to maintain the temperature below 40°. Distillation of the filtered mixture gave 8.0 g. (50%) of the silane; b.p. 75-77°.

2-Sila-2,2,6,7-tetramethyldecan-6-ol - To a Grignard reagent prepared from 0.73 g. (0.03 mole) of magnesium and 4.6 g. (0.03 mole) 2-bromopentane (Matheson, Coleman & Bell) in 50 ml. of dry ether was added dropwise with stirring 2.25 g. (0.0123 mole) of 2-sila-2,2-dimethylheptan-6-one. The mixture was refluxed for 30 min. The complex was hydrolyzed by pouring into 20 ml. of saturated ammonium chloride solution. The ether layer was washed and dried over anhydrous magnesium sulfate. After removal of the ether under reduced pressure, the crude alcohol was purified by eluting with a pentane-ether

mixture (4:1) through a dry packed column of silicic acid and infusorial earth (2:1). The infrared spectrum of this compound (pure liquid) had bands at 3450 (s), 2950 (s), 2860 (m), 1455 (m), 1375 (m), 1244 (s), 1180 (m), 1080 (w), 1040 (w), 990 (w), 925 (m), 860 (s), 835 (s), 740 (m), and 690 (m) cm^{-1}. The NMR spectrum contained peaks at 1.97 (multiplicity of 1), 1.40 (3), 0.97 (multiplet), 0.48 (8), 0.00 (1) ppm from the peak of the Me_3Si- group protons.

Anal. Calcd.: C, 67.75; H, 13.12; Si, 12.19. Found: C, 67.55; H, 13.21; Si, 12.40.

1-Methyl-2-trimethylsilylcyclobutanol - The alcohol was obtained in a 85-90% purity by microdistillation of the photolysed 2-sila-2,2-dimethylheptan-6-one at 20 mm. The purer material was obtained as the 3,5-dinitrobenzoate ester by warming the crude alcohol with 3,5-dinitrobenzoyl chloride on the steam bath for 20 min. The solid formed was extracted first with ether and water to decompose the excess chloride. The ester was recrystallized from an ethanol-water mixture (80:20 volumes) for analysis, m.p. 99-101°. The infrared spectrum (of alcohol) contained bands at 3400 (s), 2960 (s), 1600 (w), 1379 (m), 1245 (s), 1165 (m), 860 (s), 750 (m), and 690 (m) cm^{-1}. The NMR spectrum (of alcohol) contained peaks at 3.70 (multiplicity of 1, area of 1), 1.12 (m,4), 1.01 (m,3), 0.09 (1,1.5), 0.00 (1,1.5) ppm from tetramethylsilane.

Anal. (ester) Calcd.: C, 51.11; H, 5.72; Si, 7.98. Found: C, 51.28; H, 5.58; Si, 7.83.

When the yields were determined in photolysis procedure (a), the entire photolysed mixture was treated similarly with 3,5-dinitrobenzoyl chloride. The esters were separated by eluting through a silica column with pentane.

Degradation of 1-methyl-2-trimethylsilylcyclobutanol - (a) Dehydration of the alcohol. A mixture of 1.27 g. of the alcohol formed in the photolysis of 2-sila-2,2-dimethylheptan-6-one and 7 drops of 85% phosphoric acid was heated in a tube connected to a collection vessel in a carbons dioxide-acetone bath. Distillation from the heated tube gave 0.8 g. of a liquid which contained no alcohol as shown by the infrared spectrum, 3080 (w), 2850 (s), 1575 (m), 1455 (m), 1375 (m), 1246 (s), 1050 (m), 985 (w), 860 (s), 835 (s), 760 (m), 670 (m) cm^{-1}.

(b) Oxidation of the olefin. A mixture of 0.8 g. of the olefin obtained in the above dehydration and 1.5 g. of potassium permanganate in 20 ml. of water was cooled in an ice bath with stirring for 7 min. The mixture was allowed to come to room temperature. Enough 20% sodium hydrogen sulfite solution was added to oxidize all of the manganese to the manganous ion. The water layer was extracted with ether by continuous extraction for 24 hrs. After evaporation of the ether 0.2 g. of a liquid was obtained which had an infrared spectrum identical with that of levulinic acid.

Tributyltin hydride - In a mechanically stirred round-bottom flask with a nitrogen atmosphere was placed 2.70 g. (0.070 g. atm.) of lithium aluminum hydride and 50 ml. of dry ether. Then 82.2 g. (0.14 mole) bis(tributyltin) oxide was added over a period of 40 min. The mixture was stirred for 2 hrs., left overnight, and hydrolyzed with 20 ml. water. The ether layer was separated and dried over anhydrous magnesium sulfate. The ether was removed at reduced pressure. Distillation gave 65 g. (80%) of the product; b.p. 120-140° per 110 mm.

Vinyltrimethyltin - To a solution of vinylmagnesium chloride (M & T Chemicals, Inc.) in tetrahydrofuran (0.015 mole) was added immediately 3.0 g. (0.017 mole) of trimethyltin chloride in 15 ml. of dry ether. After refluxing for 30 min., the mixture was distilled. As no fraction was completely free of tetrahydrofuran, no yield is reported. The tin compound was purified by gas-liquid chromatography for spectral and chromatographic use.

Trimethyltin chloride - To 197.0 g. (1.106 moles) of tetramethyltin (M & T Chemicals, Inc.) was added over 30 min. with stirring 96.2 g. (0.368g. atm.) of tin tetrachloride (Matheson, Coleman & Bell). The reaction was heated on a steam bath for 30 min. After standing overnight, it had turned completely solid. The chloride was used without further purification.

Trimethyltin hydride - To a flask flushed with argon was added 9.43 g. (0.25 mole) of lithium aluminum hydride and 150 ml. of 1,2-bis(ethoxy)ethane (dried with sodium and distilled). The mixture was heated in an oil bath to 70°. Then, 100 g. (0.501 mole) of trimethyltin chloride dissolved in 100 ml. of the same ether was slowly added over a period of 2 hrs. The hydride was distilled as it formed into a cooled receiving flask. The temperature of the mixture had reached 125° before all of the obtainable product had distilled over at 60°. The hydride was obtained in a 89% yield (72 .7 g.).

Trimethyl-2-cyanoethyltin - A mixture of 30.0 g. (0.182 mole) of trimethyltin hydride, 19.1 g. (0.36 mole) of acrylonitrile and 1.0 g. (0.006 mole) of 2,2'-azobis(2-methylpropionitrile) was slowly warmed under argon in a water bath to 60° for 4 hrs. The reaction product mixture was filtered and the filtrate distilled through a Vigreux column (10x150 mm.

b.p. 124-125°/20 mm. The nitrile was obtained in a 70% yield (29.3 g.). The infrared spectrum of the compound (pure liquid) had bands at 2980 (s), 2930 (m), 2260 (m), 1425 (m), 1290 (m), 765 (s), and 715 (m) cm^{-1}. The NMR spectrum had peaks at 2.22 (multiplicity of 3), 1.73 (9), 0.80 (3), 0.00 (1) ppm from the peak for the Me_3Si- group protons.

Anal. Calcd.: C, 36.49; H, 6.31; N, 6.03. Found: C, 36.16; H, 6.42; N, 6.03.

5-(2-Oxopentyl)trimethyltin (XII) - A solution of 19.0 g. (0.082 mole) of 4-trimethyltinbutyronitrile in 100 ml. of ether was added dropwise to a solution of Grignard reagent prepared from 2.4 g. (0.10 mole) of magnesium and methyl bromide in 150 ml. of dry ether. The mixture was refluxed for 10 hrs. The complex was hydrolyzed by pouring on 10 g. of ammonium chloride with sufficient ice to cool the reaction. The ether layer was then removed and concentrated. The ketimine was decomposed by heating for 2 hrs. on a steam bath. The residue was extracted with ether and dried over anhydrous magnesium sulfate. Distillation through a Vigreux column (10x150 mm.) gave 5.4 g. (26% yield) of the colorless product at 60°/5 mm. The infrared spectrum of the compound (pure liquid) had bands at 2940 (s), 2800 (m), 1710 (s), 1350 (m), 1410 (m), 1185 (s), 1178 (w), 770 (s), and 710 (m) cm^{-1}. The ultraviolet spectra had $\lambda_{max.}$ 280 mμ (ε 35.2) and $\lambda_{max.}$ 219 mμ (ε 92.4). The NMR spectrum of this compound had peaks at 2.31 (multiplicity of 3), 1.9 (1), 1.65 (9), 0.90 (3), 0.45 (2), 0.07 (1) ppm from tetramethylsilane.

Anal. Calcd.: C, 38.56; H, 7.29. Found: C, 39.19; H, 7.23.

4-(2-Oxobutyl)trimethyltin (XIV) - To a Grignard reagent prepared from 2.0 g. (0.081 mole) of magnesium and

methyl bromide in 150 ml. of dry ether was slowly added 15.0 g. (0.069 mole) of 3-trimethyltinpropionitrile in 100 ml. of dry ether. The mixture was refluxed for 7 hrs. The product was worked up as in the preceding synthesis; b.p. 55-57°/5 mm. The infrared spectrum of the compound (pure liquid) had bands at 2950 (s), 2810 (m), 1710 (s), 1410 (m), 1360 (m), 1175 (w), 770 (s), and 715 (w) cm^{-1}. The ultraviolet spectrum had $\lambda_{max.}$ 280 mμ (ε 26) and 220 mμ (ε 64). The NMR spectrum had peaks at 278 (multiplicity of 3), 2.08 (1), 0.85 (3), 0.05 (1) ppm from the tetramethylsilane proton peak.

Anal. Calcd.: C, 35.71; H, 6.86. Found: C, 36.03; H, 6.60.

4-(1-Phenyl-1-oxobutyl)trimethyltin (XI) - This compound was prepared as in the preceding experiment from 1.5 g. (0.060 mole) of magnesium, 9.4 g. (0.6 mole) of bromobenzene (Fisher) and 10.0 g. (0.043 mole) of 4-trimethyltinbutyronitrile The product was microdistilled and purified by eluting through a column of 2:1 silicic acid and infusorial earth with pentane. The ketone was obtained in a 52% yield (7.1 g.). The infrared spectrum of the compound (pure liquid) had bands at 3060 (w), 2970 (s), 2920 (m), 1680 (s), 1598 (m), 1580 (w), 1450 (m), 1355 (m), 1210 (s), 1180 (w), 965 (m), 755 (s), and 685 (m) cm^{-1} The ultraviolet spectrum had a $\lambda_{max.}$ at 242 mμ (ε 12,000). The NMR spectrum had peaks at 8.00 (multiplicity of 5), 7.40 (4), 2.90 (3), 1.90 (5), 0.85 (3), 0.50 (2), 0.10 (1) ppm from tetramethylsilane.

Anal. Calcd.: C, 50.18; H, 6.48. Found: C, 50.47; H, 6.68.

3-(1-Phenyl-1-oxopropyl)trimethyltin (XIII) - This compound was prepared as in the preceding experiment from 1.34 g. (0.055 mole) of magnesium, 8.4 g. (0.055 mole) of bromobenzene, and 8.0 g. (0.037 mole) of 3-trimethyltin-

propionitrile. The ketone was obtained in a 58% yield (4.7 g.). The infrared spectrum of the compound (pure liquid) had bands at 3060 (w), 2970 (s), 1600 (m), 1585 (w), 1452 (m), 1353 (m), 1224 (s), 1280 (m), 1180 (w), 955 (m), 810 (m), 750 (s), 685 (m) cm^{-1}. The ultraviolet spectrum had a $\lambda_{max.}$ at 241 mμ (ε = 12,000). The NMR spectrum had peaks at 7.94 (multiplicity of 5), 735 (4), 313 (3), 0.98 (3), 0.50 (2), 0.10 (1) ppm from tetramethylsilane.

Anal. Calcd.: C, 48.42; H, 6.12. Found: C, 48.63; H, 6.31.

Phenyltrichlorogermane[36] - A mixture containing 13.4 g. (0.063 mole) of germanium tetrachloride (gift from Sylvania) and 6.8 g. (0.018 mole) of tetraphenylgermane was placed in an ampule which was sealed after flushing with argon. The ampule was heated at 275° for 40 hrs. in a bomb at 600 p.s.i. After removal of the excess germanium tetrachloride at reduced pressure the remaining product was used without further purification.

Phenyltrimethylgermane[36] - To a Grignard reagent prepared from 13.8 g. (0.57 mole) of magnesium and methyl bromide in 200 ml. of dry ether was added dropwise over a period of 1 hr. the contents of two ampules from the preceding experiment of phenyltrichlorogermane (0.162 mole assuming 100% yield). The mixture was refluxed for 5 hrs. Hydrolysis was achieved by pouring on 10 g. of ammonium chloride with sufficient ice to cool the reaction. After washing twice with water the ether layer was dried over anhydrous magnesium sulfate. Distillation gave 22.0 g. (79%, for the two reactions) of the germane; b.p. 148°/25 mm.

Bromotrimethylgermane[37] - To a mixture containing 21.0 g. (0.108 mole) of phenyltrimethylgermane in 15 ml. of ethyl bromide (Mallincrodt) was added 17.3 g. (0.108 g. atm) of bromine (Baker and Adamson) in 5 ml. of ethyl bromide over a period of 20 min. The mixture was refluxed for 30 min. Distillation gave 20.5 g. (96%) of the germane; b.p. 113-118° per 760 mm.

Benzyltrimethylgermane - To a Grignard reagent prepared from 3.8 g. (0.16 mole) of magnesium in 20 ml. of dry ether and 20.4 g. (0.16 mole) of benzyl chloride (Fisher) in 130 ml. of dry ether was added dropwise over a period of 30 min., 18.0 g. (0.091 mole) of bromotrimethylgermane with stirring. The mixture was refluxed for 1 hr. Hydrolysis was achieved by pouring on 10 g. of ammonium chloride and sufficient ice to cool the reaction. The ether layer was dried over anhydrous magnesium sulfate. Distillation gave 17.0 g. (90%) of the germane; b.p. 95°/25 mm.

α,α-Dibromobenzyltrimethylgermane - A mixture containing 16.5 g. (0.079 mole) of benzyltrimethylgermane and 30.3 g. (0 17 mole) of N-bromosuccinimide (Fisher) in 70 ml. of chloroform was heated. To the refluxing mixture was added 0.05 g. benzoyl peroxide. After refluxing for 3 hrs. an equal amount of the peroxide was again added. The total reflux time was 22 hrs. During this time the mixture became quite red in color. After distillation of most of the chloroform, the succinimide was removed by filtering. Distillation gave 15 g. of a fraction boiling at 69-90°/1 mm. consisting primarily of benzyl bromide and bromotrimethylgermane. Another fraction, 6.0 g., distilled over the range of 95-140°/1 mm. This mixture, containing some of the dibromide, was used without further purification.

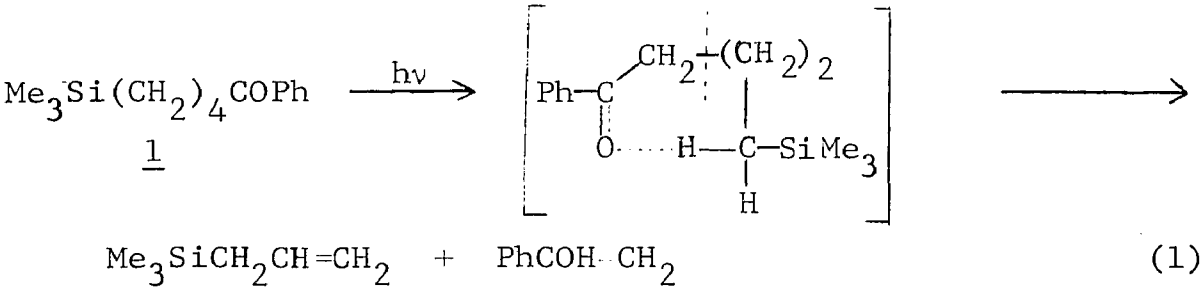
Benzoyltrimethylgermane - To the higher boiling mixture from the above experiment was added 6 ml. of 95% ethanol, 3 ml. of acetone, 2 ml of water, and 5 g. (0.03 g. atm.) of silver acetate with stirring. The mixture was allowed to stand with occasional stirring for 20 hrs. After filtering and removal of most of the solvent at reduced pressure, the remainder was extracted with ether and dried over anhydrous magnesium sulfate. Distillation gave 0.5 ml. of a bright yellow liquid. The gas-liquid chromatogram using silicone oil 200 showed the mixture to contain only 30-40% of the ketone. The infrared spectrum of this compound contained bands at 3025 (w), 2960 (m), 2850 (m), 1700 (m), 1625 (m), 1590 (m), 1485 (s), 1395 (m), 1375 (m), 1235 (m), 1205 (m), 1165 (w), 1065 (s), 1007 (s), 825 (s), 800 (s), 750 (w), and 685 (w) cm^{-1}.

SUMMARY

The purpose of this research was to explore the photochemistry of some acyclic ketones containing silicon and tin atoms. Ketones with the general structure shown below, with R = methyl or phenyl and x 1,2,3, or 4 for the silanes and 2 or 3 for the organotin compounds, were studied.

$Me_3Si(CH_2)_xCOR$ $\qquad\qquad$ $Me_3Sn(CH_2)_xCOR$

The products and yields for the silanes are given in Table I. Several types of reactions were observed. First, there is the Norrish Type II reaction. It consists of the cleavage of the molecule forming lower molecular weight ketones and olefins. An example of this reaction can be seen in the photolysis of ketone 1.



$Me_3SiCH_2CH{=}CH_2$ + $PhCOH{-}CH_2$ (1)

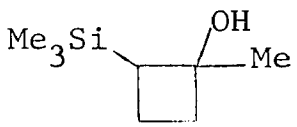
A requirement for this reaction is the presence of a hydrogen atom gamma to the carbonyl. The Norrish Type II reaction is the dominant route for the photolysis of ketones 1, 2, and 3. With ketone 2 there is also some cleavage between the carbons alpha and beta to the carbonyl. This is evident from the formation of 1,2-dibenzoylethane. Reaction with solvent, Eq. (2), leading to alcohols was of less importance with these

ketones. Ketone 3 formed a substantial quantity of a cyclobutanol through an intramolecular reaction, Eq. (3).

$$Me_3Si(CH_2)_3COCH_3 \xrightarrow[RH]{h\nu} Me_3Si(CH_2)_3\overset{\overset{OH}{|}}{\underset{\underset{R}{|}}{C}}CH_3 \qquad (2)$$

RH = solvent

$$Me_3Si(CH_2)_3COCH_3 \xrightarrow{h\nu} \qquad (3)$$



With ketone 5, cleavage between the carbonyl carbon and the carbon of the chain containing the silicon atom is the major reaction.

$$Me_3Si(CH_2)_2COCH_3 \xrightarrow{h\nu} Me_3SiCH{=}CH_2 + (CH_3CH_2CH_2)_2 + CH_3COCOCH_3 \qquad (4)$$

Ketone 4 forms alcohols by reacting with solvent and undergoes cleavage at the carbonyl group in the same direction as 5.

Photocatalyzed solvolysis was observed with ketones 6, 7, and 8. Although these compounds were quite unreactive under anhydrous conditions, when water was present they reacted very rapidly giving the products shown in Eq. (5) and (6).

$$Me_3SiCH_2COPh + H_2O \xrightarrow[ether]{h\nu} Me_3SiOH + PhCOCH_3 \qquad (5)$$

$$Me_3SiCOPh + H_2O \xrightarrow[ethane]{h\nu} (Me_3Si)_2O + PhCHO \qquad (6)$$

Most of the carbonyl compounds formed in the primary reactions reacted further giving other products.

The results from the photolysis of the organotin compounds are given in Table II. Cleavage of carbon-tin bonds

was the major reaction of ketone 11 exemplifying the cleavage reactions of all four compounds.

$$Me_3Sn(CH_2)_3COCH_3 \xrightarrow{h\nu} (Me_2Sn)_n + CH_4 + \text{polymeric products} \quad (7)$$

The Norrish Type II reaction was detected with compounds 10 and 11. The products were minor, and appeared only when the ketones were photolysed in Pyrex apparatus.

$$Me_3Sn(CH_3)_3COPh \xrightarrow{h\nu} Me_3SnCH{=}CH_2 + PhCOCH_3 \quad (8)$$

With ketone 10, there was also evidence of cleavage between the carbons alpha and beta to the carbonyl from the 1,2-dibenzoylethane detected.

TABLE I

Summary of the Photolysis Products of the Silanes

No.	Compound	Solvent	Products yields
1	$Me_3Si(CH_2)_4COPh$	Cyclohexane	$Me_3SiCH_2CH=CH_2$, (58-67%); $PhCOCH_3$, (52-61%); small quantities of unidentified alcohols.
2	$Me_3Si(CH_2)_3COPh$	Cyclohexane	$Me_3SiCH=CH_2$, (66-69%); $PhCOCH_3$, (71-75%); $(PhCOCH_2)_2$, (10-13%); small quantities of unidentified alcohols.
3	$Me_3Si(CH_2)_3COCH_3$	Pentane	$Me_3SiCH=CH_2$, (39-42%); $Me_3SiCHCH_2CH_2C(OH)Me$, (18-21%); $Me_3Si(CH_2)_3COH(Me)R$[a], (13%); CH_3COCH_3, (trace)[c].
4	$Me_3Si(CH_2)_2COPh$	Cyclohexane	$Me_3Si(CH_2)_2COH(R)Ph$[b], (10%); $Me_3SiCH_2CH_2R$[b], (6%); other unidentified alcohols.
5	$Me_3Si(CH_2)_2COCH_3$	Cyclohexane	$Me_3SiCH=CH_2$, (33-39%); $Me_3SiCH_2CH_3$, (14-17%); $CH_3COCOCH_3$, (8-12%); $(Me_3SiCH_2CH_2)_2$, (29-36%).
6	Me_3SiCH_2COPh	Ether with water	Me_3SiOH, (95-100%); $PhCOCH_3$, (10-15%)[c].

TABLE I continued -

No.	Compound	Solvent	Products yields
7	$Me_3SiCH_2COCH_3$	Ether with water	Me_3SiOH, (95-100%); CH_3COCH_3, (trace).[c]
8	$Me_3SiCOPh$	Ethanol with water	$(Me_3Si)_2O$, (90-95%); Me_3SiOEt, (5%); PhCHO, (0-20%).[c]
9	$\emptyset SiH_2CH_2CH_2CHO$	Cyclohexane	No alcohols were formed.

[a] R is a 1-, 2-, or 3-pentyl group.

[b] R is a cyclohexyl group.

[c] Most of this product was destroyed during the photolysis experiment.

TABLE II

Summary of the
Photolysis Products of the Tin Compounds[a]

No.	Compound	Products yields
10	$Me_3Sn(CH_2)_3COPh$	Me_2Sn (15-16%)[b], CH_4 (34-36%), $Me_3SnCH{=}CH_2$ (15-24%), $PhCOCH_3$ (34-39%), $(PhCOCH_2-)_2$ (10%), $(PhCOHMe-)_2$ (10%).
11	$Me_3Sn(CH_2)_3COCH_3$	Me_2Sn (40-42%)[b], CH_4 (67-71%), $Me_3SnCH\ CH_2$ (6%) .
12	$Me_3Sn(CH_2)_2\ COPh$	Me_2Sn (21-23%)[b], CH_4 (39-41%).
13	$Me_3Sn(CH_2)_2COCH_3$	Me_2Sn (38-43%)[b], CH_4 (63-69%).

[a] In cyclohexane

[b] These yields are actually the yields of dimethyltin oxide obtained by oxidation of the dimethyltin.

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